Review

Heterogeneous electro-Fenton and photoelectro-Fenton processes: A critical review of fundamental principles and application for water/wastewater treatment

Soliu O. Ganiyu[a,*], Minghua Zhou[b], Carlos A. Martínez-Huitle[a,c,*]

[a] Laboratório de Electroquímica Ambiental e Aplicada, Instituto de Química, Universidade Federal do Rio Grande do Norte, Lagoa Nova, CEP 59.072-900, RN, Brazil
[b] Key Laboratory of Pollution Process and Environmental Criteria (MOE), Tianjin Key Laboratory of Urban Ecology Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, China
[c] Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128, Mainz, Germany

ARTICLE INFO

ABSTRACT

This exhaustive review focuses on the fundamental principles and applications of heterogeneous electrochemical wastewater treatment based on Fenton's chemistry reaction. The elementary equations involved in formation of hydroxyl radical in homogeneous electro-Fenton (EF) and photo electro-Fenton (PEF) processes was presented and the advantages of using insoluble solids as heterogeneous catalyst rather than soluble iron salts (heterogeneous electro-Fenton process) (Hetero-EF) was enumerated. Some of the required features of good heterogeneous catalysts were discussed, followed by the mechanisms of catalytic activation of H_2O_2 to reactive oxygen species (ROS) especially hydroxyl radical ($\cdot$OH) by heterogeneous catalyst in Hetero-EF system. Extensive discussion on the two configuration of Hetero-EF system *vis-à-vis* added solid catalysts and functionalized cathodic materials were provided along with summaries of some relevant studies that are available in literature. The solid catalysts and the functionalized cathodic materials that have been utilized in Hetero-EF wastewater treatment were grouped into different classes and brief discussion on their synthesis route were given. Besides, the use of solid catalysts and iron-functionalized cathodic materials in bioelectrochemical system (BES) especially bioelectro-Fenton technology (BEF) using microbial fuel cells (MFCs) with concurrent electricity generation for Hetero-EF treatment of biorefractory organic pollutants was discussed. In the final part, emphasis was made on the challenges and future prospects of the Hetero-EF for wastewater treatment.

1. Introduction

Electrochemical advance oxidation processes (EAOPs) based on Fenton's chemistry are among the most widely applied advanced oxidation processes (AOPs) for the removal of persistence organic pollutants (POPs) [1–6]. These eco-friendly techniques possess some exciting advantages such as high versatility, excellent efficiency, high amenability and environmental compatibility, which distinguish them from other AOPs [5–11]. In general, EAOPs based on Fenton's chemistry utilizes hydroxyl radical ($\cdot$OH) produce from Fenton's reaction between *in-situ* generated or externally added hydrogen peroxide (H_2O_2) and Fe^{2+} ions (Eq. (1)) for the degradation of POPs. The prominent

members of this class of EAOPs are electro-Fenton (EF) and photo-electro-Fenton processes (PEF) [4,12–14]. The PEF is a photo-assisted upgrade of EF process which utilizes either ultra-violet (UVA and UVC), solar or visible light photoexcitation of Fe^{3+} complexes formed in Fenton's reaction (Eq. (1)) to produce both Fe^{2+} and $\cdot OH$ (Eqs. (3) and (4)), thus it increases the quantities and regeneration of $\cdot OH$ as well as the efficiency of the process [1,4,15,16]. The photogenerated Fe^{2+} ion can subsequently catalyzed the Fenton's reaction, forming Fe^{3+} and closing the cycle (Eq. (1)).

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \tag{1}$$

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \tag{2}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \tag{3}$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R\cdot \tag{4}$$
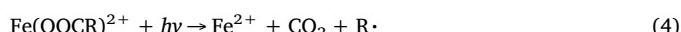
These processes are efficient for the complete degradation and excellent mineralization of synthetic and real wastewater contaminated with different class of organic pollutants such as pharmaceuticals and personal care products, endocrine disrupt compounds, pesticides, textile effluents, polycyclic aromatic hydrocarbons, surfactants and landfill leachates [1,5,7–9,12,14,16–18].

The major challenge of both EF and PEF is that both processes are only optimum at strong acidic pH conditions (*i.e.* pH 2.8–3.5), which are negative and disadvantageous from the environmental point of view, since a final neutralization step may become necessary to obtain tolerable effluents [19–22]. Besides, efficiency of EF and PEF significantly reduced when working outside pH 2.8–3.5. For instance at pH ≤ 2.5, the formation of peroxonium ions ($H_3O_2^+$) which makes the electrogenerated H_2O_2 electrophilic and reduces its reactivity towards Fe^{2+}, in addition to the preferential H_2 evolution at the cathode occurs at lower acidic pH; whereas at pH ≥ 4.5, there is both gradual precipitation of Fe^{3+} (elimination of the catalyst) as ferric hydroxide and the decomposition of generated H_2O_2 into water and O_2, thus hindering the production of $\cdot OH$ [1,19]. Other challenge of homogeneous EF and PEF is the non-recyclability of the catalyst used, which made the technique unsuitable for continuous experimental process (Table 1).

Hetero-EF uses solid catalyst source for the decomposition of H_2O_2 to form $\cdot OH$. It has been investigated as a promising alternative to homogeneous EF to overcome necessities for catalyst quantity optimization as well as widening the pH range at which EF process can be performed. This is beneficial because most real effluents encounter in nature are of wide and variable pH ranges and compositions, thus not suitable for EF and PEF treatments without adjusting the pH to strong acidic pH values [19]. Earlier effort to overcome the challenge of narrow pH window in EF resulted in the use of some naturally occur iron bearing minerals such as goethite and magnetite as heterogeneous catalysts for the treatment of synthetic wastewater [23,24]. Besides,

some of these iron minerals are pH regulator, meaning that they are capable of reducing the pH of the solution towards the strong acidic pH required for effective EF process [22,25]. In particular, pyrite and chalcopyrite has been successfully used to catalyze the degradation of some pharmaceuticals at circumneutral pH with higher removal and mineralization efficiency [25–28]. Many researches have also been tailored towards developing Fe-containing synthetic heterogeneous catalysts which are either used alone or supported on microporous or mesoporous materials for application in Hetero-EF treatment of organic pollutants in water [29–31]. Of recent, iron and/or transition metal oxides modified or functionalized cathodic materials have been prepared *via* various techniques for application in Hetero-EF process. In this case, the cathode performs dual function – as counter electrode as well as the iron source (catalyst) during the electrochemical treatment process. The functionalized cathode may be obtained by: (i) supported or immobilized iron source on a conductive materials (mostly carbonaceous material), (ii) chemically modified a conductive materials with iron source or (iii) one-pot or multistep chemically prepared low density porous solid materials containing iron and/or transition metals source (*i.e.* carbon aerogel) [19,20,32,33].

Generally, the degradation of organic pollutants during Hetero-EF involves two mechanisms – homogeneous catalyzed process by Fe^{3+}/Fe^{2+} redox couple dissolved into the solution and surface catalyzed process at the solid catalyst-liquid interface, depending on the working pH and nature of the catalyst used [19–21]. Up to date, comprehensive reviews on the Hetero-EF wastewater treatment are limited in literature. The only available chapter of a book on this topic recently published by Oturan group [22] mainly focuses on solid catalyst/supports solid catalyst without addressing the heterogeneous particle electrode and functionalized cathodic materials. Therefore, in this *exhaustive* review, the advantages of Hetero-EF and its main mechanism of production of $\cdot OH$ were firstly presented, followed by the general features of good heterogeneous catalyst. The two main configurations of Hetero-EF that have been reported in literature were extensively discussed and a summary of relevant studies related to each configuration were presented. In the final section, current challenges and possible future strategies were discussed from the perspective of catalyst development/synthesis and process design. It is in our view that this review we increase the attention given to Hetero-EF for wastewater treatment and bring about further expansion of knowledge in this exciting area of electrochemical wastewater treatment.

2. Advantages of heterogeneous electro-Fenton process

Considering the challenges of homogeneous EF process for the remediation of organic pollutants, the most important advantage of Hetero-EF is its application over a wide pH range. In essence, several

Table 1

Comparison of advantages and drawbacks of Heterogeneous EF (Hetero-EF) and Heterogeneous PEF (Hetero-PEF) with other EAOPs.

Technology	Advantages	Drawbacks
Hetero-EF/Hetero-PEF	Efficient over wide pH working window Easy post treatment separation, reusability and recyclability of the catalysts Possible regulation of solution pH towards strong acidic region Easy automation Suitable for the treatment of real wastewater	Possible additional cost due to solid catalyst production Requires more careful materials/catalysts selection to avoid negative environmental impacts
Homogeneous EF/PEF	Low quantity and cheaper catalyst source Easy to operate compared to Hetero-EF/Hetero-PEF	Efficient only at narrow pH window (pH 2.8–3.5) Requires post-treatment neutralization of treated wastewater Limited reusability and recyclability of the catalyst neutralization
Electrooxidation/Anodic oxidation	Requires no catalyst and less chemicals for operation Efficient over wide pH window Suitable for the treatment real wastewater provided non-active electrode is utilized	Higher electrical energy consumption Requires very expensive electrode material (i.e. BDD) Inferior efficiency compared to analogous EF/PEF and Hetero-EF/Hetero-PEF

Table 2
some real wastewater/effluent with their pH.

Type of real wastewater	pH range
Building and construction chemical factory	6.1–9.5 [34]
Plastic shoes manufacturing factory	5.6–7.8 [34]
Industrial dyeing effluent - Poland	11.2 [35]
Textile wastewater – India	10–12.2 [36]
Pharmaceutical wastewater	3.9–9.2 [37]
Olive oil mill wastewaters	4.5–6.5 [38]
Petrochemical wastewater	≈5.6 [39]
Landscape water	7.2 [40]
Brewery wastewaters	7.5 [41]
Alcoholic wastewater	4.5–4.8 [42]
Wastewater from almond industry	6.2 [43]
Reverse osmosis concentrate	8.3 [44]

Hetero-EF configuration and design have been reported to be practically pH independent. The circumventing of the pH limitation of classical EF process can ensure the easy application of Hetero-EF to wide range of real effluents without prior pH adjustment. Indeed, real wastewater or effluents are not only multi-components but also have wide pH variation depending on the industrial setup or origin. The pH of real effluents from some industrial plants and municipal wastewater are summarized in Table 2.

As seen in Table 2, majority of the effluents from industrial plants are either at strong basic or circumneutral pH, thus, homogeneous EF is not appropriate for the treatment of these wastewaters without prior pH adjustment. However, Hetero-EF is well suitable and efficient treatment technique for such pH-multi-variant effluents either as a single or mixture from different plants since the efficiency of most Hetero-EF design are pH independent. Based on previous studies [19–21], the independence of the efficiency of Hetero-EF has been achieved *via* to mechanisms: (i) using pH regulator as heterogeneous catalyst in the presence of O_2 and (ii) surface catalytical decomposition of H_2O_2 to ·OH. In the case of pH regulator, the catalyst undergoes oxidation in the presence of O_2 with the accumulation of H^+ in the solution, thus decrease the solution pH towards the acidic values required for efficient EF process. The most common example of such catalyst is natural pyrite and chalcopyrite, which act as both iron ions source dosage and pH regulator and the mechanism is summarized in Eqs. (5)–(8) [25,28].

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (5)$$

$$2FeS_2 + 14H_2O_2 \rightarrow 2Fe^{3+} + 14H_2O + 4SO_4^{2-} + 2H^+ \quad (6)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (7)$$

$$CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow Cu^{2+} + 17Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (8)$$
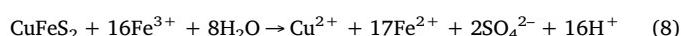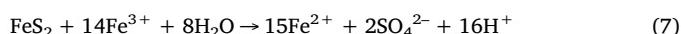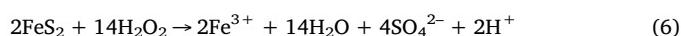
A typical pH regulating effect of natural pyrite is shown in Fig. 1 as reported by Labidha et al. [25].

On other hand, the catalytic decomposition of H_2O_2 to ·OH at the surface of solid heterogeneous catalyst has been the main mechanism of degradation of organic pollutants at circumneutral and basic pH values because iron and/or transition metal used in catalytic Fenton's reaction are indissolvable at neutral or alkaline pH conditions [20]. This implies that with solid iron/transition metal source, the Hetero-EF can be efficiently carried out over a wide pH range. In particular, iron-supported catalyst and functionalized cathodic materials such as iron/transition metal containing carbon-aerogel exhibited such properties and demonstrated to achieved excellent mineralization efficiency during Hetero-EF treatment of different class of organic pollutants over wide pH range, including strong alkaline pH conditions of around 12 [45]. Detail of the surface catalyzed decomposition of H_2O_2 to ·OH is given in the Section 3.

Related to the application over wide pH window is the elimination or inhibition of formation of iron hydroxides sludge during Hetero-EF process or post-treatment neutralization stage. This is important
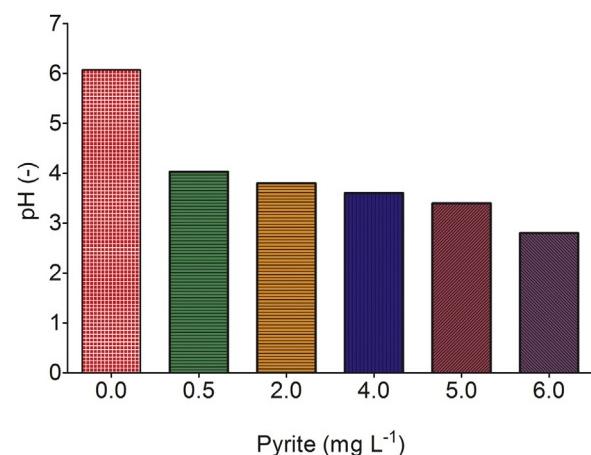

Fig. 1. Effect of pyrite suspension loading on the pH of 250 mL solution of 175 mg L^{-1} APH synthetic dye in 0.05 M Na_2SO_4 after 15 min.
Printed with the permission of Ref. [25].

because the elimination of sludge could enhance the efficiency of the process (*i.e.* increases the availability of the catalyst) as well as reduced both energy consumption and overall cost of the process [21]. The formation of the sludge during conventional EF treatment implies the loss of the Fenton's catalyst, which has adverse effect on the process efficiency, whereas sludge formed during post-treatment neutralization of solution treated with EF may require further proper disposal. The use of Hetero-EF especially with iron supported or functionalized cathodic materials eliminate the formation of the sludge during the treatment regardless of the working pH conditions. Besides, Hetero-EF using solid catalyst or functionalized cathode allows easy separation and possible recycling of the iron promoter. This is an important parameter which ensures continuous operation of the treatment system unlike in homogeneous EF where the catalyst cannot be separated from the treated solution. Indeed, some studies have shown that functionalized cathodic materials like ferrite and Fe-Cu carbon aerogel and Fe-modified carbon-felt and graphite-felt can be repeatedly used in several cycles without significant reduction in the efficiency of the process, even up to ten (10) cycles [19,20,46]. The reusability and recyclability in Hetero-EF distinguished the process from homogeneous EF and enhance the efficiency of the system. It can also reduce the overall cost for the treatment of wastewater since the process can be easily adapted to automation.

3. Mechanism of heterogeneous electro-Fenton

According to literatures [47–49], the decomposition of H_2O_2 by solid mono/mixed iron oxides, iron/transition metals containing compound and Fe-functionalized cathodic materials generally involves two situations according to the pH conditions at which electrolysis is being performed. At lower pH conditions (pH < 4.5), the process is controlled by the redox cycling of dissolved Fe^{3+}/Fe^{2+} and surface Fe^{III}/Fe^{II} couples (Fig. 2a and b). The dissolved Fe^{3+}/Fe^{2+} released from the leaching of significant quantities of iron ions for the solid catalyst or Fe – functionalized cathodic materials due to the acidic working pH conditions. Other transition metals redox couples such as Cu^{2+}/Cu^+, Co^{3+}/Co^{2+} and others could also catalyze the decomposition of H_2O_2 to ·OH if leached from solid catalyst into treated solution (Fig. 2c) [19,50–53]. Besides, the presence of other transition metals in addition to iron in the solution may provoke reduction of Fe^{3+} to Fe^{2+} in conjunction with the catalytical decomposition of the H_2O_2 as shown if Fig. 2c, thus enhance the efficiency of the electrolytic system [54–57]. At the same time under lower acidic pH conditions, H_2O_2 decomposition could also be achieved by the surface alkalescent ≡Fe^{III}/Fe^{II} –OH at the surface of the solid catalyst [58,59]. Therefore, the predominant
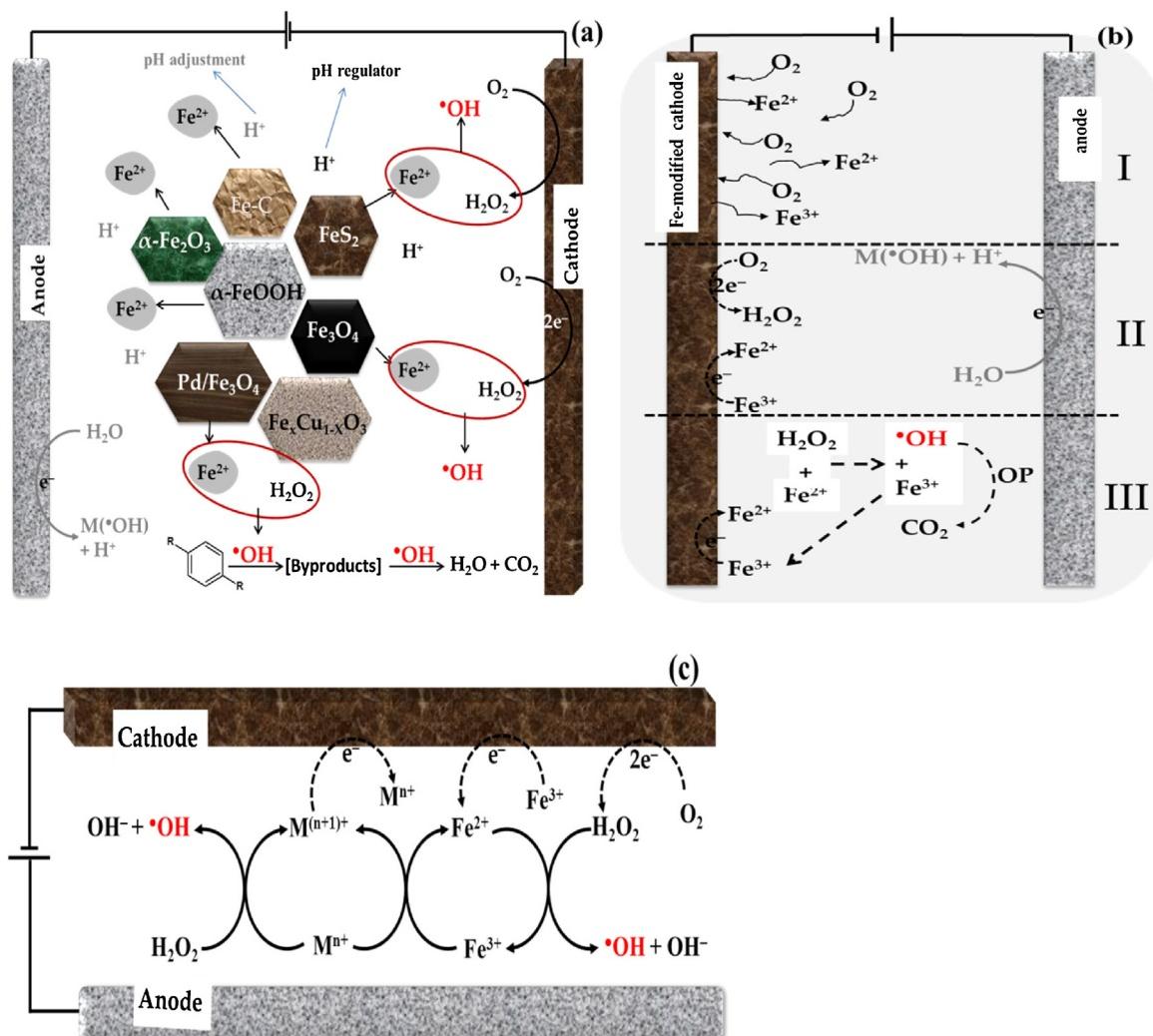
Fig. 2. mechanism of catalytic activation of H_2O_2 at acidic pH (pH ~ 3) using (a) supported or non-supported iron/iron-containing solid catalyst, (b) iron-functionalized cathodic materials (I: adsorption of dissolve O_2 and leaching of iron ions; II: electrogeneration of H_2O_2 and regeneration of Fe^{2+} from reduction of O_2 and Fe^{3+} respectively and III: Fenton's production of ·OH) and (c) proposed participation of other transition metals in redox recycling of iron ions and catalytic decomposition of H_2O_2 (M = Cu, Mn, Co, V, Ti, Ni or Nb).
Adopted from Refs. [60,21,57,83] respectively.

catalytic process not only depends on the working pH but also on the solubility of the solid catalyst at lower pH [31]. Solid catalysts such as natural iron minerals [23,27,60–62] as well as synthetic nanoparticles of iron and iron supported catalysts [21,29,58,63–74] undergoes excessive leaching of iron ions at acidic pH especially pH ≤ 3 at which Fenton's reaction is optimum, thus H_2O_2 decomposition is majorly by homogeneous Fe^{3+}/Fe^{2+} catalyzed mechanism. Depending on the cathode materials used, the homogeneous redox couples may be continuously regenerated at cathode (Eq. (9)), thus making the system a close lop [75–79].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (9)$$

Similar behavior has been reported for some iron/transition metal containing functionalized electrode such as Fe- bentonite particle electrode, Fe@Fe$_2$O$_3$/ACF, Fe-Carbon-felt, Fe and Fe-Cu allophane nanoclays with large quantities of leached iron ions, which can catalyze the H_2O_2 decomposition in the bulk with minimum surface decomposition of H_2O_2 [21,33,80–82]. It is important to note that there is possibility of oxidation of Fe^{2+} and other transition metals ions at the anode surface during the electrolysis, however, this reaction is very insignificant and rarely reported in literature.

Other functionalized cathodic materials especially iron/transition

metal containing carbon-aerogel and layered double hydroxide modified carbon-felt exhibited relatively good stability at acidic pH and the leached iron ions concentration are usually relatively minimal [19,45,84]. As such, surface catalyzed decomposition of H_2O_2 by Fe^{III}/Fe^{II} is relatively significant when those functionalized cathodic materials are utilized in Hetero-EF at low acidic pH conditions. In summary, under these circumstances, the catalytic decomposition of H_2O_2 to ·OH is by homogeneous Fe^{3+}/Fe^{2+} and surface Fe^{III}/Fe^{II} redox couple, but the predominant process is determined by the nature of the solid catalyst used (i.e. solubility with pH).

In contrast, at neutral and alkaline pH values, the contribution of dissolved iron ions to the H_2O_2 activation is expected to be negligible since Fe^{III} is insoluble [85,86]. Although the kinetics of Hetero-EF is complex and involved several parameters, but the most critical step is surely the production rate of ·OH from H_2O_2, which in this case is controlled by the solid catalyst properties, H_2O_2 generation and solution pH [87–91]. Till date, no consensus reaction mechanisms is available in literature for the entire oxidation process, however, it is widely accepted that the Hetero-EF catalysis can fit the Haber-Weiss circle mechanism, which is similar to those observed in the classical homogeneous Fenton's reaction [20,92,93]. The surface-based mechanism is summarized by reactions in Eq. (10)–(20).
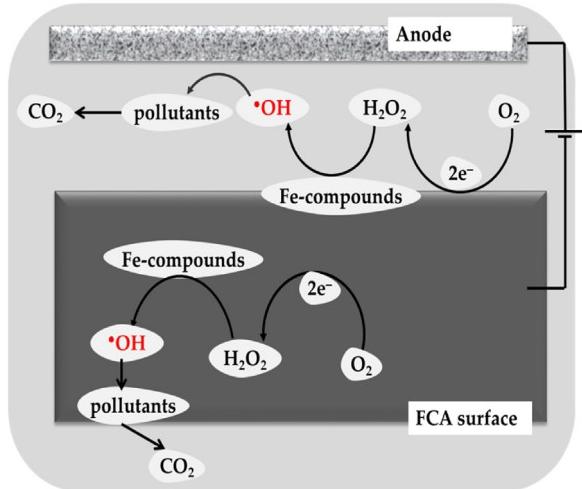
Fig. 3. mechanism of surface catalyzed activation of H_2O_2 to $\cdot OH$ at neutral and basic pH on Fe-functionalized cathodic materials (here ferrite-carbon aerogel).
Adopted from Ref. [20].

$$O_2 + 2H^+ + 2e- \rightarrow H_2O_2 \tag{10}$$

$$\equiv Fe^{III}-OH + e- \rightarrow \equiv Fe^{II}-OH \tag{11}$$

$$\equiv Fe^{III}-OH + H_2O_2 \leftrightarrow \equiv Fe^{III}-OH(H_2O_2)_{(s)} \tag{12}$$

$$\equiv Fe^{III}-OH(H_2O_2)_{(s)} \rightarrow \equiv Fe^{II}-OH(HO_2\cdot)_{(s)} + H^+ \tag{13}$$

$$\equiv Fe^{II}-OH(HO_2\cdot)_{(s)} \rightarrow \equiv Fe^{II}-OH + HO_2\cdot + H^+ \tag{14}$$

$$\equiv Fe^{II}-OH + H_2O_2 \rightarrow \equiv Fe^{III}-OH + \cdot OH + OH- \tag{15}$$

$$\cdot OH + \text{organic pollutants} \rightarrow \text{byproducts} \rightarrow CO_2 + H_2O \tag{16}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \tag{17}$$
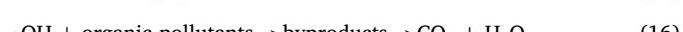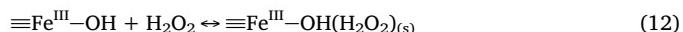
The surface-catalyzed mechanism (Fig. 3) is initiated with the generation of H_2O_2 at/within the cathode and simultaneous partial reduction of $\equiv Fe^{III}-OH$ at the surface of the Fe-containing catalyst to $\equiv Fe^{II}-OH$ by obtaining one electron (Eqs. (10) and (11)) as current is applied across the system [20,45,94]. The generated H_2O_2 can interact strongly with the negatively charged catalyst surface, forming a precursor surface complex $\equiv Fe^{III}-OH(H_2O_2)$ within the inner and outer surface of the cathode matrix [95]. More so, the surface H_2O_2 complex may be transformed into $\equiv Fe^{II}-OH(HO_2\cdot)$ via reversible ground state electron transfer from the ligand to central atom (Eq. (13)), followed by deactivation to form $\equiv Fe^{II}-OH$ (Eq. (14)) [20,61,62,92,93]. It is obvious that the rate of reactions in Eqs. (13) and (14) can be significantly accelerated by increasing the pH towards alkaline conditions, since the rapid consumption of H^+ will swiftly shift the equilibrium towards the formation of more $\equiv Fe^{II}-OH$ [30]. After that, H_2O_2 is directly and catalytically decomposed by Fe^{II} to $\cdot OH$, which can oxidize the organic pollutants until their complete mineralization to CO_2 and H_2O. The $\cdot OH$ can also react with excess H_2O_2 (quenching) to produce hydroperoxyl radical ($HO_2\cdot$) (Eq. (17)), which is a much weaker oxidant compared to $\cdot OH$, thus reducing the efficiency of the process.

Other transition metal especially Co and Cu may also catalyzed the decomposition of H_2O_2 via surface mechanism as reported for $Co^{II}Fe^{III}LDH$ modified carbon-felt [19], $Fe_{3-x}Cu_xO_4$ nanoparticles [96], Fe-Co and Fe-Cu carbon-aerogel [84,97]. It this case, $\equiv Fe^{II}-OH$ reduzate could be formed by an electron reduction of $\equiv Fe^{III}-OH$ by both $Co^{II}-OH$ and Cu^I-OH according to Eqs. (18) and (19). Additionally, direct decomposition of H_2O_2 through $Co^{II}-OH$ and Cu^I-OH catalysis to generate $\cdot OH$ could be also achieved at the surface of the transition metals-containing solid catalyst (Eqs. (20) and (21)). Overall, transition

metal-co-catalyst provided two added advantage in Hetero-EF: (i) accelerate the production of the $\equiv Fe^{II}-OH$ for H_2O_2 decomposition (Eqs. (18) and (19)) and (ii) increased the rate of catalytic decomposition of H_2O_2 to $\cdot OH$ like in the case of homogeneous EF [19,98–100].

$$\equiv Co^{II}-OH + \equiv Fe^{III}-OH \rightarrow \equiv Co^{III}-OH + \equiv Fe^{II}-OH \tag{18}$$

$$\equiv Cu^I-OH + \equiv Fe^{III}-OH \rightarrow \equiv Cu^{II}-OH + \equiv Fe^{II}-OH \tag{19}$$

$$\equiv Co^{II}-OH + H_2O_2 \rightarrow \equiv Co^{III}-OH + \cdot OH + OH- \tag{20}$$

$$\equiv Cu^I-OH + H_2O_2 \rightarrow \equiv Cu^{II}-OH + \cdot OH + OH- \tag{21}$$
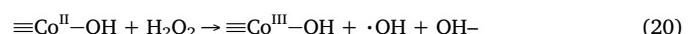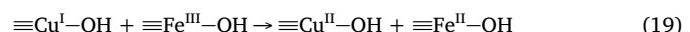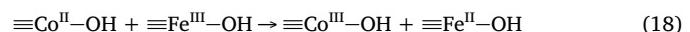
Studies have shown that the production rate of $\cdot OH$ in homogeneous Fenton reaction catalyzed by Fe^{2+} is 104–105 folds faster than Fe^{3+} catalyzed Fenton-like process [20]. On the other hand, the surface catalytic centers of Fe in iron oxide nanoparticles were reported to be at least 50-folds more effective for $\cdot OH$ generation than dissolved Fe^{3+} ions at circumneutral pH [83,101]. This implies that the reduction of Fe^{III} to Fe^{II} at the surface of the catalyst is the rate-limiting step of the whole Hetero-EF reactions [20]. Previously, Costa et al. [102] and Moura et al. [88] have drawn similar conclusions when zero valent iron (Fe°) and iron oxides encapsulated composite were studied, which had higher reactivity in oxidation of organic pollutants than Fe° or iron oxides alone due to the Fe_{surf}^{2+} species formation via electron transfer from Fe° to Fe^{3+} within the composite and increased oxygen vacancies [103]. In 2013, Wang and co-workers [20] have also shown that the formation of Fe^{II} mediator with high catalytic activity for H_2O_2 decomposition to $\cdot OH$ was via reversible redox by electron transfer among the iron species with different valences (Eq. (22)) in a ferrite-carbon aerogel containing mix phase of Fe° and α-Fe_2O_3.The higher catalytic activity of Hetero-EF process arises from the formation of more $\equiv Fe^{II}$ mediator via electron transfer among the iron species as shown in Fe° and iron oxides composite and ferrite-carbon aerogel. This can also explain the higher catalytic activity and role of Co and Cu co-catalyst in Fe/Cu and Fe/Co functionalized cathodic materials since the addition of Co or Cu led to the formation of more $\equiv Fe^{II}$ mediator as depicted in Eqs. (23) and (24).

$$\equiv Fe^\circ + 2\equiv Fe^{III} \rightarrow 3\equiv Fe^{II} \tag{22}$$

$$\equiv Co^{II} + \equiv Fe^{III} \rightarrow \equiv Fe^{II} + Co^{II} \tag{23}$$

$$\equiv Cu^I + \equiv Fe^{III} \rightarrow \equiv Fe^{II} + Cu^{II} \tag{24}$$
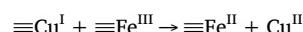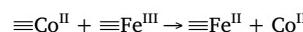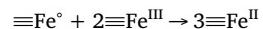
4. Required features of efficient heterogeneous catalyst

Wide varieties of substrates/materials can be selected as model catalyst and range of reaction conditions may be involved, therefore it is necessary to enumerates what would be the most important parameters that should be determined in order to rate different materials based on their activity to catalyze the decomposition of H_2O_2 in Fenton's or Fenton's-like reaction [104]. The most important parameter is the catalytic activity and stability of the material over wide experimental conditions. The material should possess good catalytic activity which must be less affected by experimental conditions, especially pH, and high stability to ensure the reusability in several runs [83,91,104–106]. It is important to note that reusability in several runs is not a good criterion to assess stability of the catalyst because pollutant-to-catalyst ratio usually determines the reusability of the catalyst [107]. This implies that for solid catalyst with high stability, large excesses quantities would allow possible reusability of the catalyst in several consecutive reactions runs, whereas less amount of solid catalyst may make reusability more difficult. Optimization of the quantities of the catalyst may be necessary because excess material could enhance the destruction of the generated $\cdot OH$ by its destructive attack on the catalyst especially when utilizing materials with low stability [104,108]. The optimum quantity of solid catalyst required for certain

wastewater treatment is closely related to the catalytic activity/properties of the solid, treated volume as well as organic matter content of the wastewater. The measurement of the maximum productivity of the catalyst may also be necessary considering the varieties and amount of solid catalyst used in Hetero-EF. Navalon et al. [104] has proposed a simple test in which a large excess substrate is used in a prolonged experiment until total deactivation of the catalyst. The data obtained will not only provide the maximum productivity but also information about the causes of deactivation of the catalyst. It may also necessary to wash the catalyst under alkaline conditions because the metal ions may form complexes with carboxylic acids, which are usually the final end organic products of electrochemical oxidation of organic pollutants. Besides in Hetero-PEF, the support material on which the catalysts (catalyst supported or impregnated on substrates) are deposited must be photo-resistant and non-radical scavenger to avoid degradation of the support.

Closely related to the stability of the catalysts as well as reusability is the absence of leaching of metal species from solid catalyst or deactivation/mechanical wearing of catalyst from the solid support into the aqueous phase, which is one key issue because it determines the contribution of homogeneous EF to the catalysis of the H_2O_2 [104,109,110]. Minimum concentration of metal species could be afforded in the solution because the species can act as homogeneous catalyst. In the case, where there is significant leaching or mechanical wearing of the solid catalyst, the overall catalytic activity could be the combination of the activity of the leached species and solid catalyst. This was the case observed at pH 2 for $Co^{II}Fe^{III}LDH$ functionalized carbon-felt [19,111], electrochemically prepared iron-modified activated carbon electrode [112] and other solid catalysts [113,114]. On the other hand, excessive leaching of metal species from solid catalyst may enhance the efficiency of Hetero-EF process especially at acidic pH conditions, at which Fenton's reaction is optimum, thus the system proceeds like a typical homogeneous EF process. The major disadvantage of leaching is depletion of the active metal sites in the solid catalysts which decreases the reusability, and if persisted for long time, it will cause the loss of the solid catalytic activity [104,115].

In the case of functionalized cathodic materials, the electrochemical properties of the modified material are an important parameter which can influence the performance of the Hetero-EF system. The nature and quantity of the solid catalyst grafted on the cathode material as well as the preparation route should have minimum negative effect on its conductivity since this could affect the charge transfer at liquid-solid interface and may reduce the potential of the material for production of H_2O_2. Most iron/transition metals compounds have lower conductivity than minimum required for EF cathode materials, as such reduces the electrical conductivity (increased electron-transfer resistance) of carbonaceous materials commonly used in EF when grafted or functionalized with these oxides. In most cases, the reduction in the conductivity is very significant but still within the limit required for successful electrochemical process, even though the effect of cathode modification on electron-transfer resistance depends on the compound grafted on the cathode. For instance, interfacial electron-transfer resistance (R_{ct}) for raw carbon-felt determined by electrochemical impedance spectroscopy (EIS) was 2.3 Ω but it reduced to 0.97 Ω after modification with $Co^{II}Fe^{III}LDH$ (Fig. 4), indicating a substantial reduction in electron-transfer resistance of the cathode and consequently, improving the electrochemical properties of the cathode [19]. Contrast results were observed for carbon-aerogel with the R_{ct} values of 3.8 Ω and 75.8 Ω obtained for pure and ferrite–doped carbon-aerogel respectively, demonstrating a reduction in electrochemical properties of prepared cathode [20].

Additionally, the substrate used to support the solid catalyst or the cathode material modified by iron compound should be non-reactive (physically or chemically) with H_2O_2 since the efficiency of the Hetero-EF system is not only determined by the activity of the catalyst but also on the concentration/production rate of H_2O_2. Therefore, prior
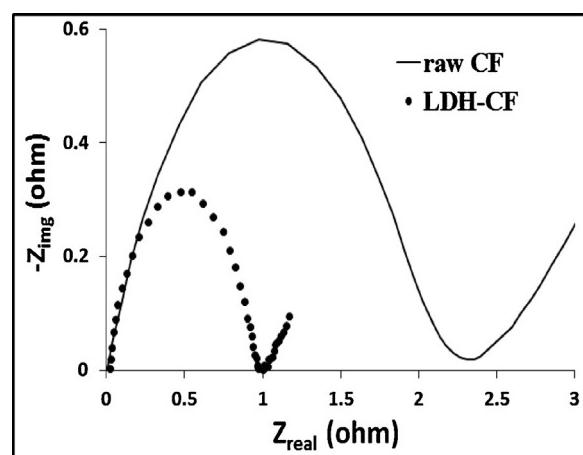
Fig. 4. EIS spectral of raw and CoFe-LDH modified carbon-felt performed in 50 mM Na_2SO_4 solution at voltage amplitude of 10 mV in the frequency range of 50 kHz to 100 MHz.
Adopted and printed with the permission of Ref. [19].

experiments are required to evaluate either the decomposition of the H_2O_2 by the substrate used as support for the catalyst and products formed or the capacity of functionalized cathodic material for production of H_2O_2.

Further, the toxicity and environmental compatibility of the solid catalyst are other important parameters that should be considered for materials selected as catalysts or as supports for the catalyst. Iron oxides and supported Fe-compounds are considered more environmental friendly and exerted no toxicity in environment; as such leaching of iron ions into the solution and its subsequent disposal and the residual solid catalyst into surface water and/or environment has limited environmental consequences to ecosystem. However, recently other transition metals like copper, manganese, vanadium, nickel and cobalt have been used along with iron/iron oxides as solid catalyst in Hetero-EF [96,116]. In this case, the disposal of the treated solution or the residual solid catalysts may have serious environmental implications since these metals ions are considered toxic especially cobalt. Therefore, careful selection of catalyst/support materials is needed to avoid use of materials with questionable environmental compatibility as solid catalyst/support in Hetero-EF system. Additionally, exclusive description of the preparation procedure and explicit characterization data are other parameters that should be considered in order to ensure reproducibility of the material and the catalytic performance [104]. The catalyst/supported catalyst or functionalized cathodic materials for Hetero-EF should have easy production or fabrication route as well as a cost effective for possible adaption on commercial scale. Studies on catalyst/supported catalyst or functionalized cathode materials with complex and expensive route may only end-up on laboratory or pilot scale, because treatment of organic pollutants in wastewater or recycling water system is considered as a non-profit but essential stage of production, which may only become necessary in order to comply with environment regulation of the country. As such techniques or processes with minimum cost implication are usually preferred even if it is less effective.

Finally, based on the above explanation, it is clear that to propose a material as potential heterogeneous catalyst/supported catalyst or functionalized cathodic materials, extensive studies are required to determine the experimental conditions range in which the materials can exhibit catalytic activity and stability, extent of leaching at these conditions, interaction of support with the H_2O_2 and the environmental compatibility of the solid catalyst and/or support. For functionalized cathodic materials, it is advisable to present the electrochemical properties along with description of synthesis procedures and well-founded characterization data.

5. Hetero-EF with catalytic addition

Hetero-EF process with catalytic addition utilized solid catalysts which are natural or synthetic, relatively insoluble iron or iron-containing compound with or without supported on substrate to catalyze the decomposition of H_2O_2 to $\cdot OH$. As stated earlier, the overall aim is to achieve reusability of the catalyst, easy separation after EF treatment and widening the pH window at which EF can be perform. The catalytic activity is usually the combination of homogeneous metal-ions and heterogeneous surface catalyzed process because extensive leaching of metal ions into the solution occurs especially when perform Hetero-EF at around pH 3 [22,117]. The solid catalysts that have been investigated in literature are grouped into two – natural minerals and synthetic iron-containing nanoparticles/iron-supported solid catalysts. The details of the studies are provided in Sections 5.1 and 5.2.

5.1. Natural minerals

Several studies have demonstrated the potential of some solid iron-bearing natural minerals to catalyze the decomposition of H_2O_2 to $\cdot OH$ and in turn, mineralization of different class of organic pollutants. In most cases, the systems allow expanding the working pH window to neutral media and preventing the accumulation of iron sludge. Pioneer studies investigated the viability of goethite (α-FeOOH) as a solid heterogeneous iron catalyst source for the mineralization of aqueous aniline solution in a modified EF process termed "goethite-catalyzed EF (GEF) process [23]. At optimum EF conditions, 95% mineralization was attained with the GEF process, suggesting α-FeOOH as a suitable solid iron dosage source for Hetero-EF process. Subsequent work [24] by the same group reported the catalytic behavior of other iron oxides minerals such as wustite (FeO), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) for the catalytic decomposition of H_2O_2 in both EF and PEF processes. Graphical representation of TOC removed after 5 h of EF treatment of $100\ mg\ L^{-1}$ aniline solutions with $1\ g\ L^{-1}$ of these solid catalysts or $0.5\ mM\ Fe^{2+}$ using Pt/GDE cell is shown in Fig. 5. It was observed that only wustite (62%) and magnetite (58%) achieved more TOC removal than Fe^{2+} (54%) during the EF treatment, whereas the catalytic efficiency of goethite and hematite was much lower. The trend in the TOC removal efficiency was related to the ability of the solid iron oxides to release Fe^{2+} to the bulk to catalyze the activation of electrogenerated H_2O_2 through Fenton's reaction (Eq. (1)), so the system behave as pure homogeneous EF process with the solid catalyst acts as self-regulator of iron dosage.

In a recent collaboration works between Oturan, Brillas and Ammar
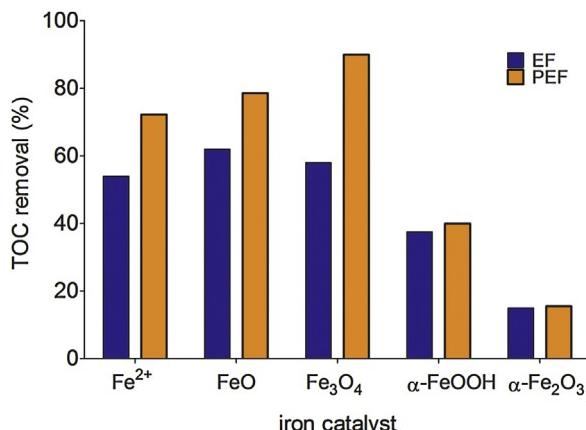
Fig. 5. comparison of TOC removal achieved after 5 h of EF and PEF treatment of $100\ mg\ L^{-1}$ aniline solutions containing $0.2\ M\ Na_2SO_4$ at pH 3, $0.5\ L\ min^{-1}$ air flow, and 250 mA applied current in Pt/GDE cell using $0.5\ mM$ of Fe^{2+} or $1\ g\ L^{-1}$ of solid iron catalyst.
Reprinted with the permission of Ref. [24].

groups, natural pyrite and chalcopyrite have been studied as a sustainable solid heterogeneous catalyst and pH regulator for the mineralization of different classes of organic pollutants [26]. For instance, Labiadh and co-workers [25] studied natural pyrite as heterogeneous solid iron dosage for the mineralization of new synthetic dye 4-Amino-3-hydroxy-2-p-tolylazonaphthalene- 1-sulfonic acid (AHPS) in an undivided reactor equipped with boron doped diamond (BDD) anode and carbon-felt cathode. The authors observed that the dissolution of the pyrite sharply reduced the pH of the solution from 6.07 to between 4.03–3.0 within the first 10 min after adding 0.5–$6.0\ mg\ L^{-1}$ pyrite; and it further decreases to 3.9–2.8 after 15 min at similar dosage using 230 mL of solution. Over 90% mineralization efficiency was attained after 5 h of electrolysis with $2.0\ g\ L^{-1}$ of pyrite dosage at applied current of 300 mA, whereas analogous studies with homogeneous EF using $0.45\ mM\ Fe^{2+}$ could only attained 70% mineralization at the same electrolysis time. Further studies by the same group [28] have shown that the addition of $1.0\ g\ L^{-1}$ pyrite dosage to aqueous solution of tyrosol adjusts easily the solution pH to around 3 and provided approximately $0.2\ mM\ Fe^{2+}$ to catalyze the so called EF-pyrite system. Comparative studies using $0.2\ mM\ Fe^{2+}$ and $1.0\ g\ L^{-1}$ pyrite dosage for conventional EF and EF-pyrite, respectively, at 50 mA, showed that the mineralization efficiency attained by EF-pyrite was approximately 5.8 times higher than that obtained in conventional EF. The superior efficiency of EF-pyrite was attributed to the "self-regulation" of the Fe^{2+} ions in the system by the pyrite as explained in Section 2. In related studies, the EF-pyrite process was also investigated for the mineralization of antibiotics levofloxacin [27], sulfamethazine [26], tetracycline [61,118] and phenolic compound, vanillic acid [119] with the TOC removal efficiency always higher for EF-pyrite compared to conventional EF, at similar experimental conditions for the pollutants studied. In particular, the mineralization efficiency obtained in EF-pyrite with Pt was quiet similar to those attained in convention EF with BDD anode during the treatment of sulfamethazine, which is very exciting consider the cost of BDD anode (Fig. 6a). The group [60] also shown that complete detoxification of sulfamethazine and tetracycline could be achieved at optimum experimental conditions and the pyrite itself have exhibited no toxicity/inhibition to bacteria V. fischeri used in microtox® analyses (Fig. 6b).

5.2. Synthetic iron/iron-containing nanoparticles/supported solid catalysts

Synthetic iron oxides and iron-contained nanoparticles and supported solid catalysts have been investigated for the Hetero-EF treatment of different classes of organic pollutants. The mechanism of decomposition of H_2O_2 to $\cdot OH$ is similar to that of natural iron mineral catalyst, which is a combination of homogeneous catalyzed process by leached/dissolved Fe^{2+}/Fe^{3+} redox cycle from the solid catalyst and surface catalysis at the solid-liquid interface with some few exceptions. The synthesis techniques varies from one solid catalyst to other and extensive characterization of these catalysts are most studied along with their catalytic activity [91,120]. For instance, Hou et al. [29] investigated synthetic nano-Fe_3O_4 for the Hetero-EF oxidation of catechol with the aim of evaluating the effect of operating parameters such as temperature, pH, current density, catalyst loading, initial catechol concentration as well as reusability of the nano-Fe_3O_4. The degradation efficiency of catechol was found to decreases with pH, but satisfactory efficiency was still attained at pH 6. Initial catechol concentration did not affect its removal efficiency, but the efficiency increases with the Fe_3O_4 loading within the range studied (0.25–$2.0\ g\ L^{-1}$). Besides, less than 10% of reduction in degradation and mineralization efficiency was observed after 8 cycles of reuse, demonstrating the high stability and reusability of the nano-Fe_3O_4 in Hetero-EF process. Other research groups [121–125] have also utilized Fe_3O_4 nanosphere supported Pd (i.e. Pd/Fe_3O_4) as solid heterogeneous catalyst for the simultaneous generation of H_2O_2 and catalytic decomposition of H_2O_2 to $\cdot OH$ (Fig. 7). The synthesized Pd/Fe_3O_4 showed efficient mineralization of
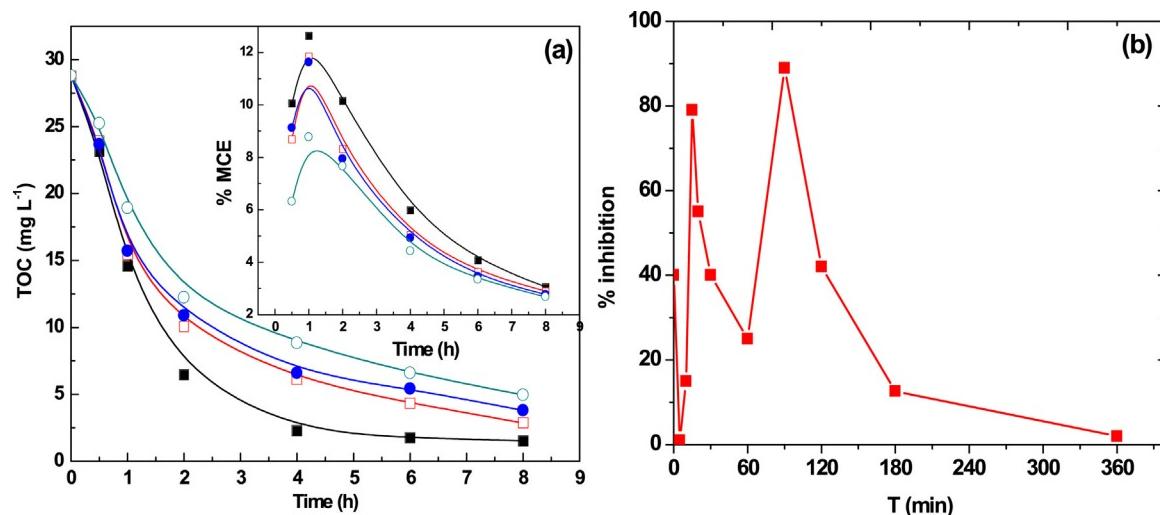
Fig. 6. (a) TOC decay *vs* electrolysis time for the mineralization of 200 mL of 0.2 mM sulfamethazine solution in 0.05 M Na_2SO_4 at pH 3, 300 mA and room temperature using undivided (●, ○) Pt/CF and (■, □) BDD/CF cells with (●, ■) 1 g L^{-1} pyrite and (○, □) 0.2 mM Fe^{2+}. The corresponding MCE is shown in the inset panel. (b) Evolution of solution toxicity assessed in terms of percentage inhibition of the luminescence of *V. fischeri* bacteria after 15 min of exposure during electrolysis at the same conditions as (a) using BDD/CF cell.
Reprinted with the permission of Ref. [26].
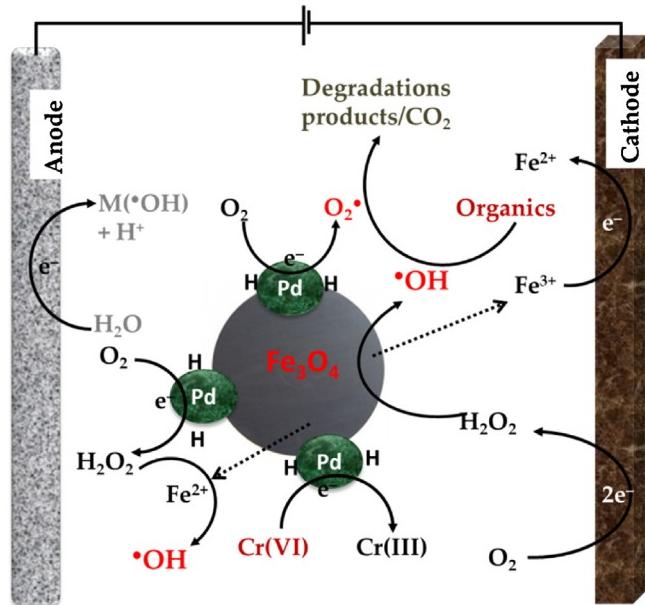
Fig. 7. Proposed mechanism of humic acids and Cr (VI) removal using Pd/Fe_3O_4catalyst.
Adapted from Ref. [122].

pentachlorophenol [124] as well as simultaneous removal of Cr (VI) and degradation of humic acids in aqueous solution [122]. Complete removal of pentachlorophenol was attained in 30 min at applied voltage of 5 V, pH 2.8 and 288 k with Pd/Fe_3O_4 compared to 17.2% obtained with electrochemical oxidation treatment alone; and approximately 90% of mineralization of humic acids and higher Cr (VI) removal efficiency was attained at the optimal experimental conditions. The Pd/Fe_3O_4 nanocatalyst acts as electron and hydrogen atoms transfer carrier and the oxidation of organics was performed by the participation of $O_2\cdot$ and $\cdot OH$, whereas the reduction of Cr (VI) was attribute to the contribution of Pd/Fe_3O_4 nanocatalyst and the atomic hydrogen on the catalyst surface (Fig. 7). The Pd nanoparticles anchor on the Fe_3O_4 nanosphere was found to enhanced the atomic hydrogen and H_2O_2 production and in turns Cr (VI) and humic acids removal efficiency up to 5 wt%, whereas no essential change in efficiency was found at higher

Pd loading. Meanwhile, the catalytic activity of the Pd/Fe_3O_4 deteriorated severely with use due to difficulty in recovery of the nanoparticles, thus limited the reusability of the catalyst. The catalyst has also been studied for the degradation of phenol [123], 4-bromophenol [121], Rhodamine B [126] and trichloroethylene in groundwater [127]. Other studies have utilized nanostructured Pd/Fe modified graphene [128] and Pd/Fe nanoscale particles [129] for degrading chlorinated phenols. In most cases, the Pd nanoparticles catalyzed the combination of H_2 and O_2 electrogenerated at the cathode and anode respectively to H_2O_2 according to Eqs. (25)–(28) [122–124,130], which is an important reagent for Fenton's reaction.

$$H_2 + O_2 \overset{Pd}{\to} H_2O_2 \qquad (25)$$

$$H_2O_2 + O_2 \overset{Pd}{\to} H_2O + {}^{1/2}O_2 \qquad (26)$$

$$H_2O_2 + H_2 \overset{Pd}{\to} 2H_2O \qquad (27)$$

$$O2 + e- \overset{Pd}{\to} O_2^{\cdot -} \qquad (28)$$

Some authors have also studied Fe_2O_3/supported-Fe_2O_3 nanoparticles or solid catalysts for Hetero-EF degradation of organic pollutants. For example, Yue et al. [131] investigated α-Fe_2O_3/γ-Al_2O_3 nanocatalyst for degrading 500 mg L^{-1} of Acid Red 3R and the decolorization efficiency of 77.2% was attained in 100 min at optimum conditions of pH 3, 0.2 $m^3 h^{-1}$ airflow and 20 V applied constant voltage. The LC–MS analysis of the treated solution showed that the azo dye was firstly degraded into aromatic intermediates, followed by ring opening into carboxylic acids before final mineralization to CO_2. Recently, Ozcan and co-workers [132] reported the efficiency of Fe_2O_3 modified kaolin for Hetero-EF degradation of antibiotic enoxacin. The mineralization rate of enoxacin attained its maximum value at 0.3 g Fe_2O_3-kaolin loading, pH 2.0–3.0 and applied current of 300 mA. Interesting, complete mineralization of enoxacin were also obtained at pH 5.1 and 7.1 and less than 0.5% reduction in mineralization efficiency was observed after 5 cycles of reuse, demonstrating the efficiency of the catalyst over wide pH range and it high recyclability.

Two Chinese research groups have also studied iron containing perovskite-like solid catalysts $ZnFe_2O_4$ [133] and $Bi_2Fe_4O_9$ [134] for the Hetero-PEF and Hetero-EF degradation of benzotriazole and 1-diazo-2-napthol-4-sulfonic acid, respectively. Heterogeneous PEF using $ZnFe_2O_4$ showed high catalytic activity for degrading benzotriazole

with 91.2% and 85.3% for degradation efficiency and COD removal, respectively, after 180 min of treatment at optimum experimental conditions with graphite electrodes. The benzotriazole degradation efficiency and COD removal decreased with an increase in pH and initial benzotriazole concentration; but increased with $ZnFe_2O_4$ dosage in the range of $0–0.067\,g\,L^{-1}$ and applied negative voltage between $–0.3$ to $–0.6$ V. Similar results were observed during the Hetero-EF process in a reactor equipped with Ti/GDE electrodes using $Bi_2Fe_4O_9$ as catalyst, however, the degradation efficiency of 1-diazo-2-napthol-4-sulfonic acid and COD depletion depended on the solution pH, $Bi_2Fe_4O_9$ dosage and applied current. At optimum conditions, almost complete COD removal (89%) was achieved after 200 min of treatment, whereas comparative electrochemical oxidation (without $Bi_2Fe_4O_9$) and adsorption (with $Bi_2Fe_4O_9$) studies merely attained 39% and 32% COD removal, respectively, at similar treatment time. Other group [95] has also investigated the catalytic activity of $Fe_{3-x}Cu_xO_4$ ($0 \leq x \geq 0.25$) nanoparticles prepared by co-precipitation method for the Hetero-EF treatment of amaranth food dye solution at strong alkaline conditions (pH 13.4) in a three-electrode cell that consists of GDE as working electrode and Pt and Ag/AgCl as counter and reference electrodes, respectively. The degradation and mineralization of the azo dye was solely by surface catalyzed process without contribution from homogeneous catalysis since the catalyst is insoluble at the working pH. Almost complete color removal and degradation efficiency (98%) and high mineralization efficiency (70%) was achieved after 90 min of treatment at 0.15 mM dosages and $–1.1$ V applied voltage.

Similarly, Zhou's group [135–137] have studied Fe-C modified by polytetrafluoroethylene (PTFE) as solid catalyst for Hetero-EF degradation of 2,4-dichlorophenol (2,4-DCP) at circumneutral pH with much emphasis on the influence of operating factors on degradation and mineralization of the pollutant, mechanism of degradation and degradation pathway. The catalytic activity of the Fe-C was well maintained after PTFE coating with much lower iron leaching; and the degradation efficiency of 2,4-DCP exceeded 95% within 120 min of treatment at current intensity of 100 mA, initial pH 6.7 and $6\,g\,L^{-1}$ catalyst dosage. A synergetic effect between anodic oxidation at the surface of the Ti/RuO_2-IrO_2 and heterogeneous catalysis on the single Fe-C was observed for the degradation and mineralization of the 2,4-DCP (Fig. 8). The catalytic activity of PTFE modified Fe-C was highly stable and there was only negligible reduction in 2,4-DCP degradation efficiency over 15 cycles of consecutive runs with relatively low iron leaching ratio. Meanwhile, Ramírez et al. [138] utilized Fe – supported on Nafion membrane and ion-exchange amberlite and purolite resin as a catalyst in PEF process for degradation of aqueous orange-II dye solution. While up to 60% TOC removal was achieved under experimental conditions employed, the Fe was relatively fixed on the supports with

limited desorption.

Some studies have utilized solid Fe-containing compound in bioelectrochemical system/bioelectro-Fenton technology (BES/BEF) using microbial fuel cells (MFCs) [139,140]. In MFC, the biooxidation of organic substrate in the anode chamber by microorganisms produces electrons that are transfer *via* external circuit to the cathode, where it reduces electron acceptor mostly oxygen to H_2O_2 [141–143]. The flow electrons produced electricity in the circuit due to drop in potential difference (Fig. 9). In essence, MFC converts chemical energy of organic substrate to electrical energy [144–146]. By addition of suitable iron source in the cathodic chamber of MFC, the produced H_2O_2 can be catalytically activated to $\cdot OH$ in a process called bioelectro-Fenton process (BEF) (Fig. 9) [147–149], thus utilizing the produced electricity to driven electrochemical system. Several studies have reported efficient mineralization of biorefractory organics in the cathode chamber of MFCs using BEF along with concurrent production of electricity.

For instance, efficient removal of p-NP was reported by Tao et al. [139] in BEF using a dual chamber MFC with continuous injection of limonite (α-FeOOH) powder into the cathode chamber as main source of iron dosage. Up to 96% of p-NP (0.25 mM) was removed in 6 h at optimal conditions and a limonite dosage of 112 mg per 50 mL of p-NP (0.25 mM) was found to sustained 7 cycles of BEF operation with p-NP removal efficiency > 94%. The mechanism of degradation of p-NP was by $\cdot OH$ generated from catalytic decomposition of H_2O_2 electrogenerated at the carbon-felt cathode by homogeneous Fe^{2+} released into the bulk *via* partial dissolution of α-FeOOH. Other studies related to Hetero-EF with iron/iron-containing nanoparticles and supported iron catalysts including BES/BEF are summarized in Table 3.

6. Heterogeneous electro-Fenton with Fe-functionalized cathodic electrodes

Fe-functionalized cathodic materials have been recently developed for application in heterogeneous electrocatalytic oxidation of refractory organic pollutants. In this context, the functionalized material serves dual purpose of electrode as well as the catalyst source in Hetero-EF system. In many cases, the catalysts are impregnated or loaded on materials with higher capacity to generate H_2O_2, such as active carbon/fiber, carbon-felt, graphite felt, and recently carbon aerogel. The catalytic performance in most cases is due to combination of both homogeneous oxidations in the bulk of the solution because of leaching of the catalyst and heterogeneous oxidation at the surface of the cathode at low pH values, whereas surface catalyzed process is predominant as pH increases (as explained in Section 3). However, the properties of the Fe-functionalized cathodic material especially the chemical stability in acidic solution play a key role in determine the contribution of the
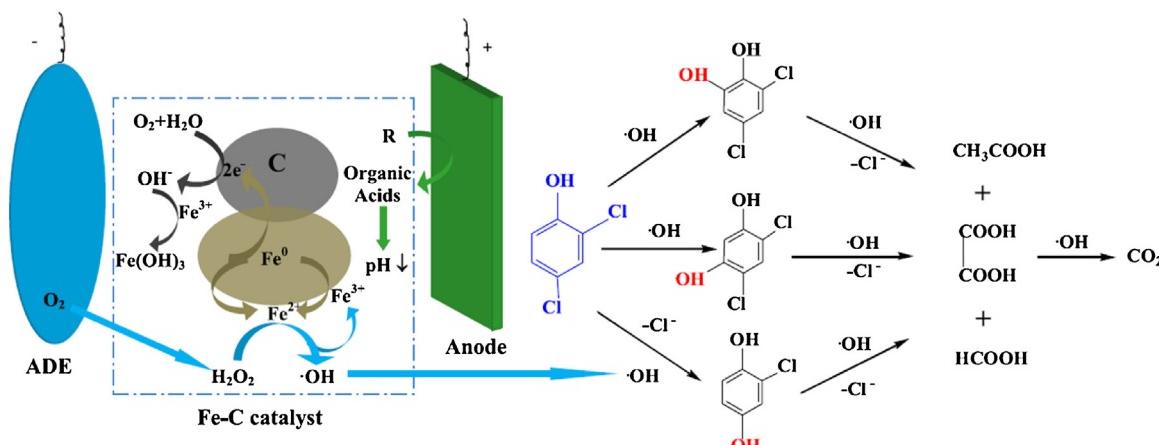
Fig. 8. Proposed mechanism and degradation pathway of 2,4-DCP during the Hetero-EF treatment using Fe-C catalyst. Reprinted with the permission of Ref. [136].
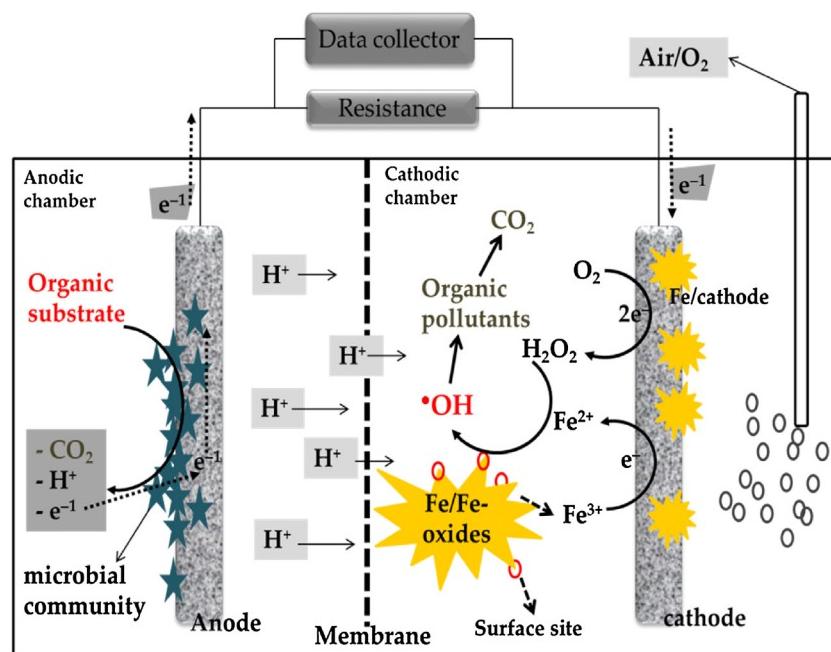
Fig. 9. Microbial fuel cell-bioelectrochemical system (bioelectro-Fenton process) for the concurrent generation of electricity and heterogeneous EF treatment of organic pollutants.
Adopted from Ref. [139] with modification.

homogeneous EF in the overall mineralization of organic pollutants during Hetero-EF process. Additionally, the efficiency, stability and reusability of the catalyst impregnated electrodes/functionalized cathode are largely affected by the technique by which the catalyst is grafted onto the carbon matrix. The technique used controls the adhesion and mechanical wearing of the catalyst from cathode matrix. Several Fe-functionalized cathodic materials have been reported in literature with widely varying properties and synthesis/preparation techniques/routes, as such there is no consensus or generalized method to obtain the functionalized cathodic materials. However, based on the existing literature, these functionalized cathode materials can be broadly grouped into three classes according to the nature of the bulk material on which the Fe/Fe-containing compounds is loaded. These groups are: Fe/supported Fe- containing particle electrodes, Fe/Fe-containing compound modified carbonaceous cathode and Fe/Fe-transition metals carbon-aerogel and are discussed vividly in the next three sections.

6.1. Fe-particle electrodes

Several studies have reported the use of 3D Fe-containing particle electrodes for heterogeneous electrochemical treatment of refractory organic pollutants. In most cases, the particle electrodes with high activity and stability are packed in between the anode and cathode of electrochemical cell for the degradation of the pollutants. The particle electrodes have been also demonstrated to enhance the conductivity of the solution and the mass transfer of substances during electrolysis [171]. Fe/Fe-compounds supported on mesoporous materials especially clay minerals are the most studied particle electrodes reported in literature, majorly because clay materials are largely abundant and inexpensive as a support material. Liu and co-workers [171] studied Fe-Ni foam particle electrodes for 3D EF treatment of RhB solution using Ti/RuO₂-IrO₂ and activated carbon as anode and cathode, respectively. The 3D EF system was able to achieve higher RhB removal efficiency (99%) compared to analogous electrochemical system (without Fe-Ni foam) (33%) and EF system (13%) at neutral pH conditions in 30 min. The enhanced degradation efficiency was attributed to the production of more ·OH in the 3D EF system because the Ni-foam particle

electrodes could activate molecular oxygen to produce (O₂·)– via a single electron transfer to subsequently generate more H₂O₂ and in turn ·OH. Synthetic RhB solution has been also treated by 3D EF using iron-slag/clay particle electrodes in a micro-electrolysis cell equipped with Pt anode and stainless steel cathode [172]. The particle electrodes with particle size 3–5 cm was prepared from pot milled steel slag powder mixed with clay and pore forming agent and calcinated at 1050 °C for 30 min. The 3D EF treatment of RhB solution with the iron-slag/clay particle electrodes could achieve 82.4% and 65.45% removal efficiency with or without the airflow in 60 min. Additionally, the particle electrodes was found to exhibited satisfactory cyclic performance over 8 cycle of reuse. A typical degradation scheme involving particle electrodes and removal efficiency of Fe-Cu allophane clay particle electrodes for the mineralization of phenol are shown in Fig. 10a and b respectively.

A Chinese group has also studied a neutral 3D EF system with various bentonite-based Fe particle electrodes for the degradation of phenol [80], Acid Orange II [174] and pulp and paper mill wastewater [175]. The group showed that at optimal condition and pH 6.24, Fe₃O₄-bentonite, Fe₂O₃-bentonite and Fe°-bentonite could achieve 13.28%, 57.8% and 67.48% COD removal respectively after 4 h of treatment of phenol solution. Analysis of the Fe leaching behaviors from the particle electrodes during the degradation of phenol revealed that both homogeneous and heterogeneous EF reactions contributed to the degradation of the phenol. Similar results were reported for Fe-bentonite particle electrodes for the degradation of Orange II with COD removal and decolorization efficiency of 71.57% and 98.89%, respectively [174]. Other relevant studies on the application of Fe-particle electrodes for 3D heterogeneous EF degradation of organic pollutants are summarized in Table 4.

6.2. Fe-functionalized carbonaceous cathode material

Fe-functionalized cathode based on carbonaceous materials are the most widely studied functionalized cathodic materials for Hetero-EF treatment of organic pollutants because of the high capacity of carbonaceous materials for the in-situ production of large quantities of H₂O₂ (Fenton reagent) during electrolysis. Indeed, several studies and

Table 3
Summary of some relevant studies on Hetero-EF system catalyzed by Fe/Fe-supported solid catalysts.

catalyst	pollutants	electrodes	Technology operation conditions	main results
Iron rich sludge	1,4-dioxane	Ti/RuO₂/SS	EF	undivided glass stirred tank reactor connected to Peristaltic pumps; 1000 mL solution; $j = 2.8$ A cm^{-2} for 120 min; pH 2.0–3.0	5.3 mM 1,4-dioxane removed at current efficiency over 70% [150]
Fe-AB	Lissamine green B Azure B	Gr	EF	undivided cylindrical glass reactor; 150 mL solution;14.19 V applied potential for 30 min; 8.69 Fe –AB; pH 2–8.	98–100% removal efficiency for both dyes; catalytic activity unchanged after 3 cycles [151]
		Gr	EF	airlift continuous flow reactor; 1500mL solution; 115 g Fe-AB; 1.5L-min^{-1} air flow; 3 V constant voltage; pH 2	81% and 87% decolorization for Lissamine green B and Azure B respectively [152]
	Imidapricloprid	BDD/Gr	EF	undivided glass reactor; 150 mL solution; 5 V constant voltage for 30 min; 4.27–16.84 g Fe-AB; pH 2 – 7.	98–100% removal efficiency in successive batches; efficiency decreases with increased pH and Fe-AB dosage [153]
	Indole	Pt/CF	EF/PEF	undivided closed glass reactor; 250 mL solution; $j = 0.13 – 0.8$ mA cm^{-2}, 50 – 250 mg L^{-1} Fe-AB; pH 3; 25 °C	90% TOC removal in 7 h at pH3, 0.53 mA cm^{-2}, and 200 mg L^{-1} Fe-AB; UVA-PEF only achieve slight increase inefficiency [31]
	Reactive Black 5	Gr	EF	undivided glass reactor; 150 mL solution; 5.69 V constant voltage; 2.68 mM of Fe-AB beads; pH 2.24	65% COD removal [154]
Mn-AB	Reactive Black 5	Gr	EF	undivided cylindrical glass reactor; 150 mL solution; 5 V constant voltage; 6–14 g Mn-AB dosage; pH 2	75% removal efficiency after120 min; stable catalytic after four cycle of reuse [155]
Mn-AB, Fe-AB, and Fe-AC	Winery wastewater	BDD/Ni-foam	EF	undivided cylindrical glass reactor; 150 mL solution in 0.01M Na₂SO₄; 15 V constant voltage; 1 L min^{-1} air flow; 8.7, 14.25 and 3 g of Fe-AB, Mn-AB and Fe-AC respectively; natural pH	56%, 54% and 82% COD removal efficiency for Fe-AB, Mn-AB and Fe-AC respectively after 24 h [156]
Iron oxide- allophane clay	Atrazine	Pt/GC	EF	three electrode undivided glass reactor; 8 mL of 46 mM atrazine solution; −1.04 V constant voltage; pH 3–6; 25 °C	100% and 76% removal efficiency at pH 3 and 6 respectively [81].
Fe-sepiolite	Reactive Black 5	BDD/Gr	EF	undivided reactor; 150 mL of 100 mg L^{-1} Reactive Black 5 solution; 3 g Fe-sepiolite; 5 V constant voltage; pH 2	97.2% decolorization after 90 min; stable catalytic activity after 4 cycle [157]
Fe-Y zeolite/ Alginate	Imidapricloprid and chlorpyrifos	BDD/Gr	EF	undivided reactor; 150 mL solution; 5 V constant voltage; air flow rateof 1 L min^{-1}, 50–700 mg L^{-1} Fe-Y zeolite; pH 3	98% removal efficiency in 120 min; low reusability but can be enhanced by embedded the Fe-Y zeolite in alginate [158]
Fe₃O₄ NPs	RB 19	Pt/ACF	EF	undivided cylindrical glass reactor; 200 mL of 100–300 mg L^{-1} of RB19 in 0.05 M Na₂SO₄ solution; 1.0 g L^{-1} Fe₃O₄ NPs; $j = 3$ mA cm^{-2} and pH 3	87% TOC removal efficiency in 120 min [159]
	4,6-dinitro-o-cresol (DNOC)	Gr	EF	undivided cylindrical cell; 200 mL of 11.4 µg L^{-1} of DNOC in 0.08 M Na₂SO₄ solution; 1 g of Fe₃O₄; I = 0.025 A; O₂ flow of 40 mL.min^{-1}	100% removal of DNOC in less than 60 min at pH 2.8 [160]
rGO-Fe₃O₄	Methylene blue	Ni-foam	EF	undivided reactor; 150 mL of 10 mg L^{-1} solution; I = 0.5 mA; O₂ flow rate of 40 mL.min^{-1}; 30% wt rGO- Fe₃O₄; pH 2	97% decolorization after 24 min [131]
Pd-Fe₃O₄	phenol	Pt	EF	undivided reactor; 200 mL of 20 mg L^{-1} solution; 1 g L^{-1} Pd/Fe₃O₄; I = 50 mA; pH 3; 25 °C	98% degradation efficiency in 60 min; stable catalytic activity over ten cycle of reuse [123]
Pd-Fe	MTBE	Ti/IrO₂-Ta₂O₅	EF	undivided cell; 400 mL of 20 mg L^{-1} solution; 2 mA cm^{-2}; pH 3; 25 °C	70% removal efficiency in 20days [125]
Fe-AC	m-cresol	BDD/Ni-foam	EF	undivided glass reactor; 150 mL of 100 mg L^{-1} m-cresol solution; 28 mg L^{-1} Fe in Fe-AC; air flow rate of 1 L min^{-1}; 5 V constant voltage; pH 3	83% TOC removal in 2 h; removal mechanism was by adsorption onto Fe-AC followed by oxidation [161]
α-Fe₂O₃ and α-Fe₂O₃/ TiO₂ NTs	Phenol	Ni/TiO₂ NTs	PEF	undivided glass reactor; 100 mL solution of 10 mg L^{-1} phenol solution; 5 V constant voltage; pH 3	100% phenol removal in 60 and 120 min for dispersed α-Fe₂O₃ and fixed α-Fe₂O₃/TiO₂ NTs respectively [162]
CuO/γ-Al₂O₃	Amaranth	Pt/AQS-PPy	EF	Undivided electrolytic cell; 200mL of 80 g L^{-1} amaranth in 0.1 M Na₂SO₄ solution; 1.25 g L^{-1} of CuO/γ-Al₂O₃; – 0.4 V cell voltage; pH 4.3	56.35% TOC removal efficiency after 5 h [163]
Fe scrap	p-NP	CF	BEF	divided glass reactor; 300 mL of 1mM p-NP; 10 g of scrap iron; pH 2	complete removal of p-NP in 12 h and 85% TOC decay in 96 [164]
FeVO₄	Orange II (AO7)	C-cloth/CF	BEF	divided glass reactor; 200 mL of 50 mg L^{-1} of AO7 solution; 1 g of FeVO₄ powder; pH 3	89% and 81% AO7 and COD removal efficiency respectively [165]
γ-FeOOH	AO7	PPy-AQDS/CF	BEF	divided glass reactor; 75 mL of 0.2 mM of AO7; 1 g L^{-1} of γ-FeOOH; pH 7	Higher H₂O₂ electrogeneration and complete mineralization of AO7 in 60 h [166]

113

Applied Catalysis B: Environmental 235 (2018) 103–129

substantial review works [4,79,183–185] have detailed the structural and physicochemical properties of most carbonaceous materials as electrodes for energy and environmental applications. They possess some distinguished characteristics such as good electronic conductivity and mechanical stability, excellent chemical stability, high surface areas and porosity which can provide abundant redox reaction sites and excellent electrolytic efficiency at relatively low cost [79,186–188]. Their high abundance in nature, inexpensive and easy accessibility make them most studied cathode materials in electrochemical waste-water treatment. Additionally, carbon is nontoxic and exhibits a high over-potential for H_2 evolution and low catalytic activity for H_2O_2 decomposition [4,189]. Three dimensional carbonaceous materials, such as, activated carbon felt/fiber (ACF), graphite felt (Gr), carbon-PTFE O_2 diffusion (GDE) and carbon-felt (CF) are the most widely used material for the preparation of Fe-functionalized cathode due to their high ratio of surface area to volume, combined with high mechanical stability which is necessary for effective modification process [190]. Several modification methods at different experimental conditions have been reported for the preparation of Fe-functionalized carbonaceous cathode for the application in Hetero-EF treatment of organic pollutants. After modification process, the electrochemical activity of the carbon material could be significantly changed [19]. As stated earlier in Section 1, the Fe- functionalized carbonaceous materials acts as cathode or working electrode in the electrolysis cell on which dissolved oxygen is reduced to produce H_2O_2 as well as iron source for the release of Fe-species required for the activation of H_2O_2 to ·OH. Besides, the mechanism of the decomposition of H_2O_2 to ·OH depends on the properties of the solid iron source loaded on the cathode and the working pH of the solution.

The functionalized cathode materials have been used both in conventional Hetero-EF as heterogeneous catalyst system and bioelectro-Fenton's system in MFCs for degradation of biorefractory organic pollutants. Especially worth nothing is the pioneer works which utilized $Fe@Fe_2O_3$/CNT as an effective oxygen-fed gas diffused cathode for a neutral EF system [63]. The $Fe@Fe_2O_3$ nanowire was first synthesized by reaction between $FeCl_3$ and $NaBH_4$. The $Fe@Fe_2O_3$/CNT cathode was prepared by mechanical rolling of paste made from a mixture of $Fe@Fe_2O_3$, CNT, and PTFE suspension in ethanol to form a 0.5 mm thin electrode. The prepared electrode was found to be efficient for H_2O_2 electrogeneration; and the degradation of RhB with this electrode was 91.5% in 120 min at neutral pH conditions, demonstrating that the system was very promising for wastewater treatment. Subsequent studies by the same group investigated $Fe@Fe_2O_3$/ACF cathode because ACF can easily adsorb iron ions that can be reduced to $Fe@Fe_2O_3$ by $NaBH_4$ [165]. It was found that the Hetero-EF system with $Fe@Fe_2O_3$/ACF cathode showed higher catalytic activity than EF systems catalyzed with commercial Fe° powders and ferrous ions (Fe^{2+}) for degrading RhB. Since then, several other studies have utilized Fe- modified ACF/AC for the Hetero-EF treatment of several pollutants such as m-cresol and RhB using iron-loaded AC [160] and methyl orange using $Fe@Fe_2O_3$/ACF cathode in bioelectro-Fenton's system with MFCs [191]. Excellent production of H_2O_2 and high catalytic activity was also reported for electrochemically prepared iron-modified AC electrodes in Hetero-EF and Hetero-PEF treatment of synthetic methyl orange solution [113]. Almost total decolorization (96%) and TOC removal (88%) was attained during Hetero-EF treatment in 30 min of treatment, whereas complete decolorization (100%) and TOC removal (98%) was achieved in similar treatment time using Hetero-PEF process.

CF electrode has a high specific surface area that favors the fast generation of both Fenton's reagent (H_2O_2 and Fe^{2+}) and can be easily modified with Fe and/Fe-containing compounds for application in Hetero-EF system. Sklari et al. [33] investigated Fe-loaded CF composites prepared under oxidizing condition by immersing the CF in ethanolic solution of $FeCl_3$.$6H_2O$ or reducing condition with continuous flow of N_2. The Fe-CF prepared under reduced condition was found to have high stability and catalytic activity during Hetero-EF process,

Table 3 (*continued*)

catalyst	pollutants	electrodes	Technology operation conditions	operation conditions	main results
Fe$_3$O$_4$-NPs	Acid red 14 (AR14) Acid blue 92 (AB92)	Gr/Gr-CNTs	EF	Undivided glass reactor; 250 mL of either AR14 or AB92 in 4 g L^{-1} Na$_2$SO$_4$ solution	93.35% and 84.46% AR14 and AB92 removal efficiency at 0.18 A; pH 3 and 1 g L^{-1} and 0.6 g L^{-1} Fe$_3$O$_4$-NPs for AR14 and AB92 respectively [167]
	Methylene blue (MB) AR14	rGO-Gr	EF	–	98% and 99% removal for MB and AR 14 respectively [168]
Fe-hydrogel	Reactive black 5 Blue Sella solid	Gr	EF	Undivided cylindrical reactor; 150 mL of dyes in 0.01 M Na$_2$SO$_4$; 5 V constant voltage; air flow rate of 2 L min^{-1}	< 96% RB 5 removal after 120 min [169]
Fe°-NPs	Phenol	SS	EF/PEF	Undivided reactor; 1 L of 200 mg L^{-1} phenol in 1 g L^{-1} of Na$_2$SO$_4$; 0.5 g L^{-1} Fe° NPs; 500 g L^{-1} H$_2$O$_2$; pH 6.2	100% phenol removal in 30 min [170]

Note: SS – stainless steel; Gr – graphite; CF – carbon-felt; GC – glassy carbon; AB – Alginate beads; rGO – reduced graphene oxide; MTBE – methyl *tert*-butyl ether; FCSW – iron contain sludge waste; GDE – gas diffusion electrode; AC – activated carbon, NTs – nanotubes, PPy-AQDS – polypyrrole-anthraquinone-2,6-disulfonate; CNTs- carbon nanotubes; NPs – nanoparticles.

Fig. 10. (a) Scheme for degrading organics by particle electrodes and (b) COD removal efficiency at pH 3 and 5 for the mineralization of 100 mL of 5×10^{-4} M phenol in 0.05 M Na_2SO_4 by Fe-Cu allophane (APN) clay with different composition of Fe and Cu ($Fe_{6-x}Cu_x$) at –0.6 V. Adopted from Refs. [173,82] for (a) and (b), respectively, with modification.

achieving diclofenac degradation and mineralization efficiency of 63.7% and 31.6%, respectively, at low applied potential of 1.0 V *vs* Ag/AgCl, pH 7 and 34 mg L^{-1} initial diclofenac solution. Similar studies was reported by Brillas group [192] where CF/iron oxide air-diffused cathode prepared by Fe^{3+} electrodeposition was utilized for the mineralization of malachite green dye in a Hetero-EF and UVA Hetero-PEF processes. It was observed that the oxidation of the malachite green at pH 3 was by hydroxyl radicals formed at the BDD anode surface from water oxidation and at the cathode or in the bulk from Fenton's reaction between the deposited or leached Fe^{2+} and electrogenerated H_2O_2 in both treatment, along with the photo-oxidation by UVA light in heterogeneous PEF. Complete decolorization of the dye was attained in both processes, whereas mineralization efficiency of 85% and 98% was achieved at 50 mg L^{-1} malachite green, pH 3 and current density of 21.7 mA cm^{-2} for Hetero-EF and UVA Hetero-PEF treatment respectively, after 6 h. Recently, we reported CoFe-layered double hydroxide (CoFe-LDH) modified CF as an efficient heterogeneous catalyst/cathode for mineralization of orange II [19]. The modified cathode synthesized by in-situ solvothermal process showed highly crystalline, porous and anisotropic CoFe LDH grown on CF (Fig. 11a–d).

Electrochemical characterization using cyclic voltammetry and EIS showed that the prepared cathode was highly stable at neutral pH conditions with almost zero percent Fe or Co leaching and good conductivity for electrochemical process. Excellent mineralization of orange II was obtained at all pH values studied and superior mineralization efficiency was always achieved in Hetero-EF with CoFe LDH/CF compared to conventional EF with added Fe^{2+} and/or Co^{2+} with relatively good reusability (Fig. 11e and f). The mineralization of orange II was *via* the formation several intermediates and carboxylic acids which were later mineralized to CO_2 (Fig. 12)

Other studies have reported Fe-modified graphite electrodes prepared with various iron sources and techniques for Hetero-EF treatment of different organic pollutants. Graphite electrodes have been extensively studied as suitable electrode (both anode and cathode) in electrochemical wastewater treatment owing to their excellent conductivity and mechanical integrity which can enhance their modification [185,193]. For instance, nanostructured iron oxide/graphite (FeOOH/graphite, Fe_2O_3/graphite and Fe_3O_4/graphite) electrodes fabricated from synthetic acid mine drainage was reported to have shown high stability and catalytic activity for the degradation of RhB in Hetero-EF system [194]. It was found that EF system using raw graphite could only achieve 30% RhB removal in 120 min whereas up to 62.5%, 94.5% and 95.6% was attained with FeOOH/graphite, Fe_2O_3/graphite and Fe_3O_4/graphite, respectively, at the same treatment time. More recently, Zhou group [46,116] investigated a novel roll-made GDE

loaded with trace transition metals (M/GDE, M=Cu, Ce, Mn, Fe, Co) as an effective cathode/catalyst for Hetero-EF (Hetero-EF-like) degradation of methyl orange. The prepared rolling-made GDE demonstrated a good catalytic activity and stability for H_2O_2 production, with a maximum H_2O_2 concentration of 595 mg L^{-1} generated after 120 min and variation of less than 3.36% after 10 cycle of reuse. Among the cathodes studied, Co/GDE showed the highest activity at Co loading of 0.7 wt% with highly stable catalytic activity towards pH variation (pH 3–9). It was confirmed that the degradation of methyl orange was majorly by ·OH produced from the catalytic activation of H_2O_2 in a Fenton or Fenton-like reaction. Table 5 summarizes some other relevant studies that have applied Fe-functionalized carbonaceous cathode materials for Hetero-EF/Hetero-PEF treatment of wastewater.

6.3. Fe-containing carbon-aerogel

Aerogel is a general term used to describe a class of material derived from organic, inorganic or hybrid molecular precursors that are normally prepared by sol-gel process and retain it three-dimensional and highly porous network after appropriate drying technology [208]. Aerogel was first developed in 1930's by S. Kistler using supercritical drying approach to extract pore-filling liquid of wet gels to obtain air filled solid structure with approximately same dimension as their initial wet gel [209,210]. Although, pioneer studies mainly focused on robust aerogels with different stating molecules, the subsequent studies investigated silica (SiO_2) type aerogels [211–214]. Due to complex and intricate multistage synthesis procedures, aerogel as a porous material was abandoned and studies about it synthesis and applications were forgotten for over 30 years. However, different types of aerogels including inorganic (*e.g.* SiO_2 derived from alkyoxysilanes, TiO_2, Al_2O_3, ZrO_2 and others) [211,215–218], organic (polyamide, polystyrene, polyurethane, *etc.*) [219,220], carbon (carbon, carbon –nanotube, graphene) [221–224], semiconductor chalcogenide [225], natural based aerogels [226–228] and SiC aerogels [222,229–232] have been developed in the last decades due to advances in synthesis and drying technologies. In general aerogel are light material with overwhelming majority of it volume being air, which endows it with interesting physicochemical properties, such as high porosity and easy to modified or functionalized for excellent mass-transfer of reactants/substances [233–235].

Carbon aerogels (CAs) were extensively developed in early 90's with multi-facet properties and additional functionality such as mechanical strength, hydrophobicity and catalytic features for high performance applications [236–239]. They possess exclusive properties such as low density (~0.003–0.5 g cm^{-3}), relatively high surface area

Table 4
Summary of some relevant studies on the application of Fe/Fe-supported particle electrodes in Hetero-EF wastewater treatment.

particulate electrodes	pollutants	electrodes	technology	operation conditions	main results
Fe-Mn – carbon black	Nitrobenzene	Pt/FMBO/ACS/CB	EF	Open, undivided glass reactor; 400 mL of 100 mg L^{-1} of NB in 0.05 M Na_2SO_4 solution; O_2 flow rate of 0.3 L min^{-1}; 8.33 mg cm^{-2} FMBO/AC loading; pH = 7	1.3 µW^{-1} cm^{-2} of ·OH produced at pH 7; 80 ± 3% and 42 ± 7% NB removal for Pt//FMBO/AC/CB and 0.1 Fe^{2+} EF respectively after 120 min [176]
Martite-particles	Paraquat	Gr/Pt	EF	Undivided glass cell; 100 mL of 20 mg L^{-1} paraquat in 0.05 M Na_2SO_4 solution; 1 g L^{-1} plasma modified martite catalyst; 300 mA applied current; pH 6	85.78% and 41.03% paraquat removal efficiency in 150 min for plasma modified and unmodified martite particles [177]
Fe-clay allophane	Atrazine	Fe-Clay-GC//Pt//Ag/AgCl	EF	Undivided cell equipped with three electrodes; 30 mL of 45 mM atrazine in 90% 0.1 Na_2SO_4 and 10% methanol solution; − 1.04 V constant voltage; pH 3–6	100% and 76% atrazine degradation efficiency attained at pH 3 and 6 respectively after 8 h treatment [81]
Fe$_2$(MoO$_4$)$_3$-kaolin 450 (FM-kaolin-450)	Methyl Orange	Gr/Gr	EF	Undivided glass cell; 300 mL methyl orange solution in 0.05 M Na_2SO_4; air flow rate of 1 L min^{-1}; pH 2 – 6.7	97% decoloration in 10 min and 92.48 COD removal in 60 min at pH 3 and current density of 68 mA cm^{-2} [173]
Fe-Cu allophane clay	Phenol	Fe-Cu-GC//Pt//Ag/AgCl	EF	Undivided cell equipped three electrodes; 100 mL of 0.5 mM phenol in 0.05 M Na_2SO_4 solution; −0.6V; pH 3–5.5	100% phenol in 2 h and 80% COD removal at pH 3 in 4 h was attained with Fe-Cu allophane [82]
Nano-Fe°/AC	Methyl orange	Pt/graphite felt	EF	undivided cell; 130 mL of 60 mg/L solution; cathode potential −0.65 V, pH = 3, O_2 flow rate 0.4 L/min	80% decolorization in 10 min, and 40% TOC removal after 2 h [178]
Fe-Slag – clay particles	RhB	Pt/SS	EF		82.4% and 65.45 RhB removal efficiency with and without particulate respectively [172]

Table 4 (*continued*)

particulate electrodes	pollutants	electrodes	technology	operation conditions	main results
				Undivided cell; 50 mL of 0.01 mM RhB in 0.1 M Na_2SO_4; 15 g of the particulate; V = 3 V	
SAC-Fe or Fe_3O_4 NPs	Coal gasification wastewater (CGW)	Ti/SnO2/ACF	EF	Undivided cell; 1 L of CGW containing 173.3 mg L^{-1} COD and 48.3 mg L^{-1} total phenol; 5.0 g L^{-1} SAC-Fe and 1.07 g L^{-1} Fe_3O_4 NPs; air flow rate of 4 L min^{-1}; pH = 6.8	78.1% and 37.1% COD removal with SAC-Fe and Fe_3O_4 NPs respectively in 2 h [179]
CTAB-bent/OH-Al-CTAB-bent	Paper and pulp mill wastewater	SS/SS	EF	Undivided tank reactor; wastewater contain 256 mg L^{-1} COD and UV$_{254}$ 4.183 cm^{-1}; working volume of 500 mL; air flow rate of 2.5 L min^{-1}; applied current of 0–3 A	84.3 % and 93% COD and color removal efficiency respectively [175]
Fe-bentonite (Fe-bent)	Orange II	Gr/Gr	EF	Undivided glass reactor; 400 mL of 100 mg L^{-1} Orange II in 0.05 M Na_2SO_4 solution; 14.29 mA cm^{-2} current density; 0.5 g PEs; pH 6.4	98.89% and 71.75% decolorization and COD removal efficiency after 1 h of treatment [174]
α and γ-FeOOH	RhB	AQ/rGO//Pt/Ag/AgCl	EF	Divided glass cell with cation exchange membrane separator; 0.01 M NaClO4 as anolyte; 200 mL of 10 mg L^{-1} RhB in 0.5M Na_2SO_4 or $MgSO_4$ catholyte; 100 g L^{-1} of PEs; Oxygen flow rate of 0.6 L min^{-1}; − 0.5 V constant voltage	100% RhB removal in 120 min [30]
Pd-Fe/Ni-foam	DMZ	Pt/Pt	EF		96.5% DMZ removal achieved in 60 min with Pd-Fe/Ni-foam PEs [180]

117

Table 4 (*continued*)

particulate electrodes	pollutants	electrodes	technology	operation conditions	main results
				Undivided reactor; 400 mL of 50 mg L⁻¹ DMZ in 5 g L⁻¹ Na₂SO₄ solution; air flow rate of 1 L min⁻¹; 12.5 g L⁻¹ of PEs; current density of 31 mA cm⁻², pH 3	
AuPd/Fe₃O₄	BMIM	DSA	EF	Undivided cylindrical glass reactor; 150 mL of BMIM containing 2.13 g Na₂SO₄ and 1.5 g of AuPd/Fe₃O₄; applied current of 300 mA; pH 3	100% removal of 10 mM BMIM in less than 40 min [181]
FCSW PE	p-NP	PbO₂/GDE	EF	Undivided reactor; 50 mg L⁻¹ p-NP in 0.05 M Na₂SO₄ solution; air flow rate of 0.2 L min⁻¹ 3 g L⁻¹ of FCSW PEs; current density 3 mA cm⁻², pH 3;	94.31% p-NP removal in 60 min and 78.96% TOC removal in 180 min [182]

Note: FMBO – Fe-Mn binary oxide; ACS – activated charcoal; CB – carbon black; SS – stainless steel; ACF – activated carbon felt; AQ – anthraquinone; DSA – dimensional stable anode; SAC – sludge derived activated carbon; BMIM – 1-butyl-3-methylimidazolium hexafluorophosphate; GDE – gas diffuse electrode; FCSW – fluffy clump steel wire; PEs – particle electrodes.
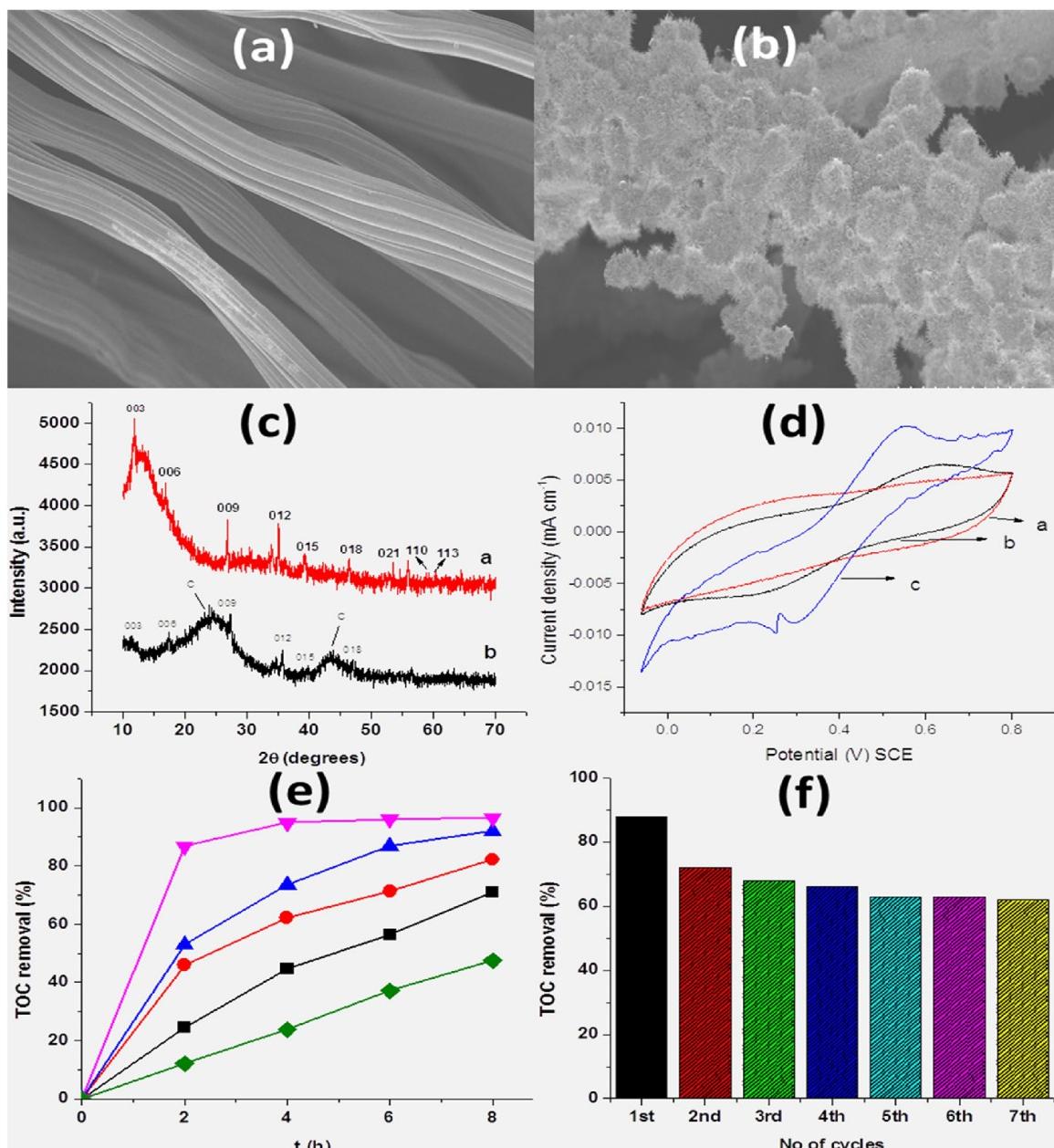
Fig. 11. SEM image of (a) raw CF and (b) CoFe-LDH/CF; (c) X-ray diffraction pattern of (a) CoFe-LDH powder and (b) CoFe-LDH/CF; (d) Cyclic voltammetry of CoFe-LDH/CF performed in 50 mM Na_2SO_4 at (a) pH 5.83, (b) pH 3 and (d) pH 2; (e) comparison of TOC removal efficiency of (♦) 0.2 mM Co^{2+}, (■) 0.2 mM Fe^{2+}, (●) 0.2 mM (Fe^{2+} + Co^{2+}) (1:1),(▲)0.2 mM (Fe^{2+} + Co^{2+}) (2:1) and (▼) CoFe-LDH/CF during the mineralization of 150 mL of 0.1 mM AO7 solution in 0.05 M Na_2SO_4 at pH 3 and applied current of –40 mA using Pt anode; and (f) TOC removal efficiency with number of cycle using CoFe-LDH/CF at similar conditions as (e). Reprinted with the permission of Ref. [19].

($\sim$500–1200 $m^2\,g^{-1}$), high porosity ($\sim$88–99.8%) with tunable surface chemistry combined with ability of being processed into a variety of morphologies and sizes to suit different applications [240,241]. CAs is a hybrid aerogels which could well combine advantages of several materials to achieve specific function. Among other properties, CAs is characterized by high electrical conductivities and good corrosion resistance especially under the strong oxidizing conditions [222,242–244]. The mechanical robustness and thermal stability of CAs could be tremendously enhanced when hybridized with iron aerogel, which is known for its strong mechanical and thermal strength. This type of hybrid aerogel, containing carbon and iron network, has been developed as a prospective candidate for catalytic applications [32,236,245]. Indeed, several studies have demonstrated the suitability of this material as Fe-functionalized cathodic material for Hetero-EF

and Hetero-PEF processes, in the last four years.

CAs is prepared by wet chemical synthesis approach, sol-gel reaction, but through different starting precursors, operating and provision requirement [214]. The complete steps involved in CAs preparation include sol-gel formation, solvent exchange, ambient pressure drying and pyrolysis (Fig. 13) [246–248]. Firstly, mixture solutions of precursors, water and catalysts are transformed into highly dispersed solution of colloidal primary particles or monomers *via* hydrolysis and polycondensation reactions to form sols. The colloidal particles of the sol can connect to one another to form three-dimensional and interconnected network upon addition of chemical cross-linker or by changing the conditions of reaction (i.e. pH, temperature) [249–252]. The formation of the porous three dimensional networks is the most critical and determinant aspect of aerogel [209]. The pore-filling solvent of the
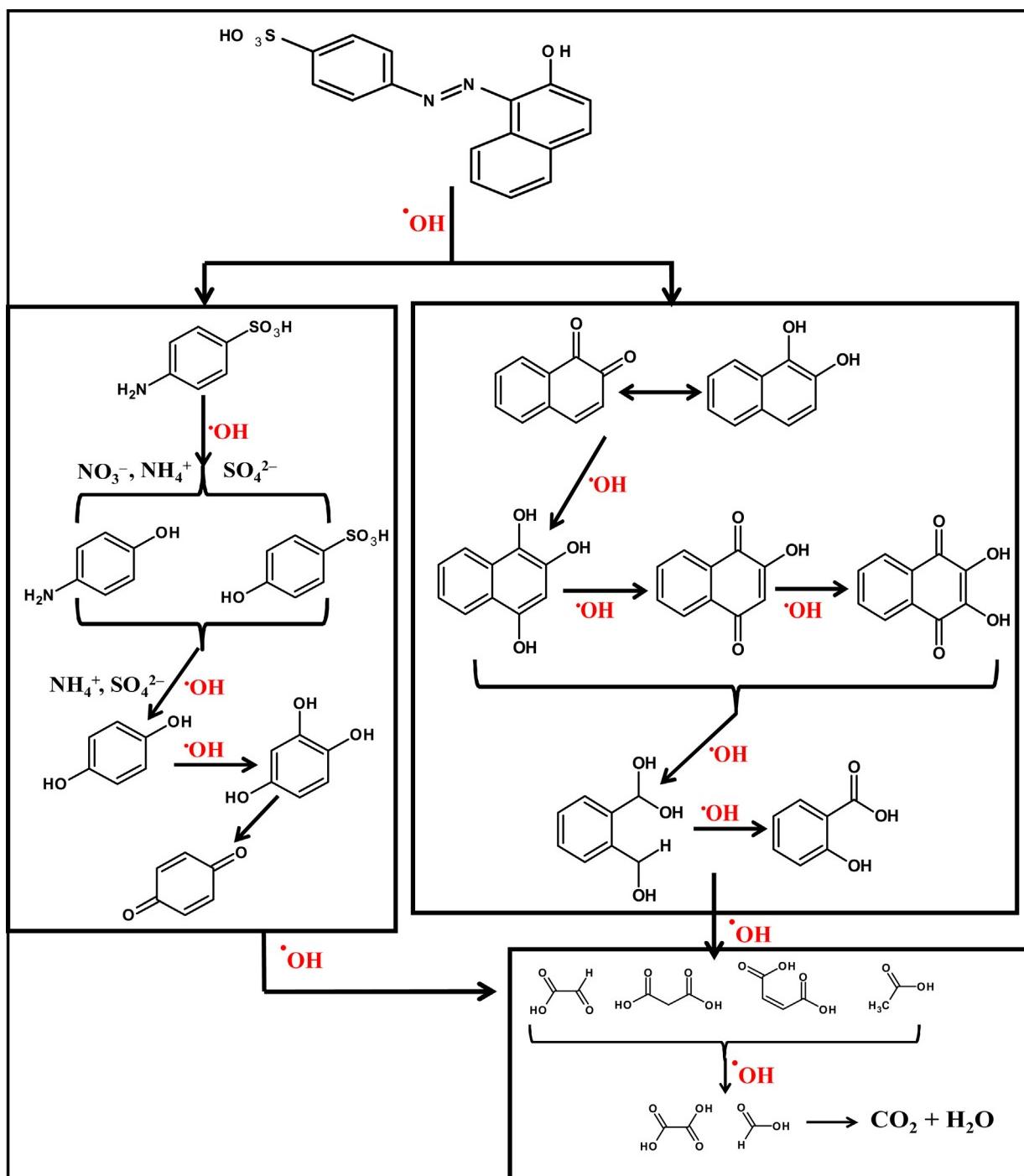
Fig. 12. Reaction mechanism for complete degradation of orange II by ·OH. Reprinted with the permission from Ref. [19].

wet gel is exchange with volatile solvent to form the highly porous network. To prepare functionalized CAs (i.e. Fe-functionalized CAs), iron/transition metal containing compounds are added to the homogeneous precursor solution prior to the formation of sol [251–255]. The wet gel is subjected to curing and ageing because the chemical reactions are not finished with gel formation [256]. In fact during the ageing, the reactive species such as −OH or unreacted monomers contained in the gelation solvent inside the pores are condensed onto the network. The curing or ageing process is commonly performed by soaking the gel in the initial sol or suitable solvent under controlled conditions (pH, time and temperature) for long period ranging from hours to days [212,246,256,257]. The 3D networks of the gel is strengthening and

coarsening and there are changes in textural properties of the gel such as pore size, porosity and surface area during the ageing process [258–262]. Drying the gel without collapsing the original porous 3D structure is a critical step in aerogel preparation process [262–265]. Supercritical drying (using alcohol, acetone, or CO_2) is the most popular conventional method for drying wet gel, but it requires reactors withstanding high pressure, which greatly increase the production cost [266,267]. Ambient pressure drying and freeze-drying are some of other prominent drying method reported in literature, however, most studies on Fe-functionalized CAs utilized ambient pressure drying, which is easy and inexpensive [268–270]. The final step of CAs preparation is carbonization of the dry gel at high temperature (> 600 ˚C)

Table 5
Summary of some relevant studies on application of Fe/transition metals modified carbonaceous cathode for Hetero-EF wastewater treatment.

Functionalized cathode	Preparation method	pollutant	technology	Operation conditions	Main results
Fe/AC	Electrochemically, using three electrode cell with AC suspended in H_2SO_4 and addition of $FeCl_3$ in drops	MO	EF/PEF	Undivided glass cell equipped with three electrodes; 25 mL of 10 ppm of MO solution; − 900 mV cathode potential; pH 3; 25 °C	EF - 96% decolorization and 88% TOC in 30 min, PEF - 100% decolorization and 98% TOC removal in 30 min [113]
Fe_3O_4/GDE	Fe_3O_4/AC was prepared by precipitation method; then mixed with PTFE, ethanol and Na_2SO_4 before forming under in hydraulic machine	Tetracycline (TTC)	EF	Undivided glass cell; 100 mL of 50 mg L^{-1} TTC in 0.05 M Na_2SO_4 solution; − 0.8 V potential vs SCE; pH 3	94.2% TTC removal in 100 min [195]
Fe_2O_3-C/graphite membrane cathode	i) pretreatment of Gr membrane; ii) deposition of active layer containing carbon black (CB) and Fe iii) deposition of reductive and protective layer using CB and PTFE	Flutriafol	EF	Flow reactor; working volume of 54.84 cm³ at 82.9 L m⁻² h⁻¹ flux; 100 mg L^{-1} of flutriafol in 0.05 M Na_2SO_4; current density of 13 mA cm⁻²; CB/Fe of 6.2: 1; pH 6.7	79.6% flutriafol removal [196]
γ-Fe_2O_3-Fe_3O_4/CF (Fe-NPs/CF)	oxidizing condition - soaking of CF in $FeCl_3.6H_2O$ and dried or reducing condition – passing N_2 into solution prior soaking	Diclofenac	EF	Flow reactor with 3 pair of anode/cathode; flow rate 40 L h⁻¹, V = 2 V per anode/cathode;	85% and 36% diclofenac and TOC removal efficiency respectively [197]
FeC_x/N-doped carbon fiber (FeC_x/NCNFs)	FeC_x was prepared by electrospinning using iron (III) acetylactonate, N,N-dimethylformamide and polyacrilonitrile solution	Dimethylarsinate (MDA)	EF	Undivided cell, 100 mL of 5 mg L^{-1} DMA in 0.05 M Na_2SO_4 solution; O_2 flow rate of 50 mL min⁻¹; applied current of 0.15 A; pH 3	96% DMA removal in 6 h with residual As (V) concentration less than 0.01 mg L^{-1} [198]
Fe_3O_4/graphite felt (Fe_3O_4/Gr)	MFC treatment of acid mine drainage using Gr anode; after operation, Gr anode was remove and calcined	RhB	EF	Undivided reactor; 175 mL of 50 mg L^{-1} RhB in 50 mM Na_2SO_4 solution; O_2 flow rate = 1.5 L.min⁻¹; pH 6.8	100% decolorization and mineralization in 10 and 70 h respectively [199]
QEEG/Fe_3O_4 composite	Co-precipitation of pre-hydrolyzed ferric and ferrous salt in the presence of QEEG	Bisphenol	EF	Undivided cell; 60 mL of 5 mg L^{-1} bisphenol in 0.05 M Na_2SO_4 solution; air flow rate = 1 L.min⁻¹; V = −1.2V; pH 3	Complete bisphenol removal in 90 min [200]
Fe_2O_3/Gr	Precipitation using $FeCl_3.6H_2O$ and $NaBH_4$ solution added in drop	Alcohol wastewater	EF	Undivided glass reactor; 250 mL of wastewater; applied current of 51.54 mA; pH 2.84	66.15% COD removal in 69.29 min [42]
Fe@Fe_2O_3/ACF	Precipitation using $FeCl_3.6H_2O$ and $NaBH_4$ solutions	MO	BES-EF	Divided reactor (MFC); 500 mL of 5 mg L^{-1} of MO in 0.05 M Na_2SO_4; O_2 flow rate of 750 mL min⁻¹; pH 3	73.9%–86.7% MO removal efficiency for eight successful cycle [191]
Fe@Fe_2O_3/CF	Precipitation using $FeCl_3.6H_2O$ and $NaBH_4$ solutions	RhB	BES-EF	Divided reactor (MFC); 75 mL of 15 mg L^{-1} of RhB solution; p H 3	95% and 90% RhB decoloration and TOC removal respectively in 12 h [201]
		Swine wastewater	BES-EF	Divided flow reactor at 3.1 or 1.24 L.day⁻¹ with organic loading 1.1 and 4.6 g COD L⁻¹ day⁻¹; pH 3	62.2%–95.7% COD removal efficiency [141]
		E2 and EE2	BES-EF	Divided reactor; 75 mL of 20 mg L^{-1} each of E2 and EE2 in 0.1 M NaCl; air flow rate of 100 mL min⁻¹; pH 3	81% and 56% removal for E2 and EE2 after 10 h [202]
Fe@Fe_2O_3/Gr felt	Precipitation using $FeCl_3.6H_2O$ and $NaBH_4$ solutions	Triphenltin chloride (TTCT)	BES-EF	Divided reactor; 30 mL of 100 mg L^{-1} of TTCT solution; air flow rate of 100 mL min⁻¹; pH 3; 30 °C	78.32 ± 2.07% TTCT degradation efficiency at rate of 0.775 ± 0.021 h⁻¹ [203]
		Medicinal herb wastewater	BES-EF	Divided cell; 450 mL of wastewater, pH 3	84.02% COD removal [204]
FeOOH/TiO_2-GAC	Sol-gel preparation of TiO_2 with addition of FeOOH/GAC	Tetracycline	BES-EF	Divided cell with MBR; 78.75 mL of tetracycline with continuous air flow	90% and 80% COD and NH_4-N removal respectively [205]
Pyrrhotite/Gr	Grafting using conductive silver paste	Landfill leachate	BES-EF	Divided cell; 250 mL of landfill leachate; pH 5.4	77% and 78% color and COD removal respectively [206]

(continued on next page)

Table 5 (*continued*)

Functionalized cathode	Preparation method	pollutant	technology	Operation conditions	Main results
CNT/γ-FeOOH	Forming at high pressure using paste made from a mixture of CNT, γ-FeOOH, PTFE and ethanol	Orange II	BES-EF	Divided cell; 75.6 mL of 0.1 mM orange II; pH 3	100% decolorization and mineralization efficiency [140]
Pd-Fe/GrO	Photo-induced reduction	4-bisphenol	EF	Divided cell; 150 mL of 100 mg L^{-1} 4-bisphenol in 0.03 M Na$_2$SO$_4$ solution; current density of 25 mA cm^{-2}; pH 7 and t = 60 min	100% and 99.5% removal of 4-bisphenol in catholyte and anolyte respectively [121]
Fe-CHI/Ni|ACF| Fe-CHI	Deposition of Fe^{2+}-CHI on Ni foam followed by fastening with elastic rope	RhB	EF	Divided cell; 5 mg L^{-1} in 0.05 M Na$_2$SO$_4$; air flow of 0.1 m^3 min^{-1}; applied current of 10 mA; pH 6.2	93% degradation in 120 min [207]

Note: QEEG – Quinone-functionalized electrochemically exfoliated graphene; BES – bioelectrochemical system; Fe-CHI – Fe-chitosan.

and ambient pressure under an inert atmosphere of N$_2$ or Ar to decompose oxygen and hydrogen moieties in the polymeric chain and enriches the network with the pure carbon moieties [271,272]. The synthesis procedure for modified CAs preparation is presented in Fig. 13.

The earlier studies on the potential of CAs in electrochemical wastewater treatment utilized CA as particle electrodes for electrocatalytic degradation of RBRX dyes [273] and synthetic phenol wastewater [244]. The CA particle electrodes prepared by ambient pressure drying technique showed excellent degradation (~98%) of RBRX and phenol as well as high catalytic stability up to 20 cycles of reuse. Most studies on application of Fe – functionalized CAs cathode for 3D Hetero-EF/PEF system were conducted by Zhao group with focus on homogeneous Fe$_3$O$_4$@Fe$_2$O$_3$ [45], ferrite [20], Fe$_3$O$_4$@C, and Fe-Cu [274] CAs. In all their studies, Fe-functionalized CAs was prepared by sol-gel formation, solvent exchange, ambient pressure drying and pyrolysis as described above and the prepared cathodes always exhibited good conductivity, high catalytic efficiency and distinguish stability. For example, Fe$_3$O$_4$@Fe$_2$O$_3$ CAs composite cathode was reported to achieve excellent efficiency for the degradation of pesticide imidacloprid during Hetero-EF treatment in pH range of 3–9. Approximately 90% imidacloprid and TOC removal was attained in 30 and 60 min of treatment respectively, at current density of 10 mA cm^{-2} and pH 3 [45]. The catalytic activity of Fe$_3$O$_4$@Fe$_2$O$_3$ CAs was satisfactorily stable with pH as the change in TOC removal efficiency values was less than 3% for treatment performed between pH 3–pH 9. Similar results were obtained during the Hetero-EF treatment of an active ingredient of conventional fungicide metalaxyl with homogeneous ferrite CA [20]. The prepared ferrite CA was able to achieve 98% of TOC elimination in 4 h at pH 3 and stable catalytic activity over ten (10) cycles of reuse at pH 6, with less than 2% difference in TOC removal (Fig. 14). The same group reported similar behavior for continuous bulk ultradispersed Fe-Cu CA cathode during the Hetero-EF degradation of MB dye with high TOC removal achieved at wide range of pH values (pH 3–9) [97]. It was demonstrated that the COD of the treated real dyeing wastewater was below China's discharge standard after just 30 min of treatment with very low power consumption (0.34 k W h per ton of wastewater). In a related study [275], Fe-Cu embedded CA was reported to have achieved efficient TOC removal (88–99%) in 240 min during the Hetero-EF treatment of dimethyl phthalate, imidacloprid, bisphenol A and perfluorooctanoate. Successful decontamination of five sanitary sewages were also exhibited by the same cathode with the residual COD less than China national discharge standard (< 50 mg L^{-1}) at low specific energy consumption. Similar results was achieved for the treatment of dimethyl phthalate (DMP) using highly ordered mesoporous Fe$_3$O$_4$@C CA with 95% and 65% DMP degradation and mineralization efficiency attained in 120 min respectively [274].

Fe-functionalized CA has also been studied as cathode material in Hetero-PEF process for the degradation of RhB and DMP using 2Fe/Co–CA [276] and imidacloprid using Fe$_2$O$_3$ –CA [92]. 100% and 80% removal efficiency was obtained at 45 and 120 min for RhB and DMP respectively in solar Hetero-PEF treatment, whereas complete degradation of imidacloprid could be only reached in 180 min under similar solar Hetero-PEF treatment. Other studies have also reported high catalytic activity and stability for iron oxide-graphene/CNT – CA composite cathode for the Hetero-EF degradation of MB [32]. The authors showed that 99% removal efficiency of MB can be achieved in 60 min at pH 3 and applied current of 15 mA using 5% Fe containing graphene/CNT – CA. In all studies that involve Fe-functionalized CA composite cathode, two mechanisms was always proposed for the activation of H$_2$O$_2$ to ·OH during the Hetero-EF process as described in Section 3, depending on pH of the treated solution. At acidic pH values, there was slight leaching of Fe and/or Cu/Co from the functionalized CA cathode into the solution, thus the activation of H$_2$O$_2$ to ·OH is controlled by cycling of Fe^{3+}/Fe^{2+} and/or Cu^{2+}/Cu^{+}//Co^{3+}/Co^{2+} redox couple in the solution and at the surface of CA cathode. However
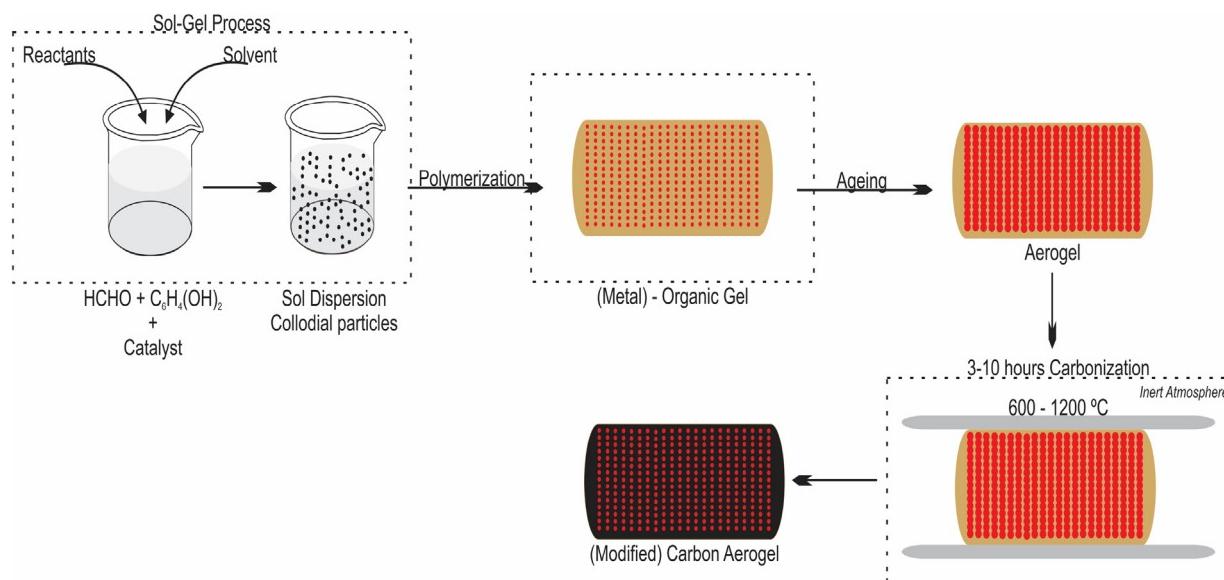
Fig. 13. Scheme for the synthesis of CAs.
Adapted from Ref. [20,208].

at neutral and alkaline pH values, only surface catalyzed activation should be predominant because Fe and or Cu/Co are not soluble at such pH conditions. Besides, photo-assisted Hetero-EF usually gives better mineralization and current efficiency compared to analogous Hetero-EF, thanks photo-degradation of carboxylic complex as well as generation and regeneration of additional ·OH and Fe^{2+} respectively from the photo excitation of Fe-complexes.

7. Challenges and future prospects

Some of the main challenges encounter in Hetero-EF/PEF are mostly related to the heterogeneous catalyst itself, especially supported catalyst and functionalized cathode used in Hetero-EF and Hetero-PEF system, though a cost-effective production of hydrogen peroxide on the cathode is essential [277,278]. Among these problems, catalyst fall-off from the support due to mechanical wearing in the solution and dissolution/excessive leaching of the catalyst at strong acidic pH are the most detrimental challenge that affects both catalytic stability and reusability efficiency of heterogeneous catalyst. Except in few cases like functionalized CAs, rolling made GDEs and some Fe-modified carbonaceous cathodes, excessive leaching or dissolution were usually observed when operating at strong acidic pH values (< pH 4), as such the overall electrolysis system is controlled by homogeneous catalysis by

recycling Fe^{3+}/Fe^{2+} redox couple. In this case, the efficiency of the electrochemical system usually depreciates significantly with increase in pH because the contribution of homogeneous EF diminishes with rise in pH conditions. Additionally, the mechanical wearing or fall-off of the catalyst from the support or cathode may increase with electrolysis time as the solution weakens the adhesive bond between the catalyst and the support regardless of operating pH values. This phenomenon was observed during Hetero-EF treatment of AO7 using solvothermal synthesized CoFe-LDH/CF cathode at pH 5.83, with mechanical fall off of the CoFe-LDH from the CF substrate after 6 cycles of 2 h repeated reuse due to the strong agitation of the solution and weakening of the bond between the CoFe-LDH and the CF [19]. The same thing could be indicated for Fe-loaded clay materials, ACF and iron sludge. However, this problem is limited or completely eliminated in functionalized CAs because the catalyst (Fe/Fe-compounds or Cu/Co) are not only embedded in the bulk of the CAs but also form the integral part of the 3D network of the CAs as explained in Section 6.3.

Agglomeration of the catalyst is another challenge that is commonly encountered in Hetero-EF and Hetero-PEF systems, especially with non-supported catalyst. Most synthetic non-supported heterogeneous catalysts such pure Fe_2O_3, Fe_3O_4 or $Fe°$ or their doped/modified form are usually prepared and used as nanoparticles, as such there are usually tendency of agglomeration of these particles with treatment time,
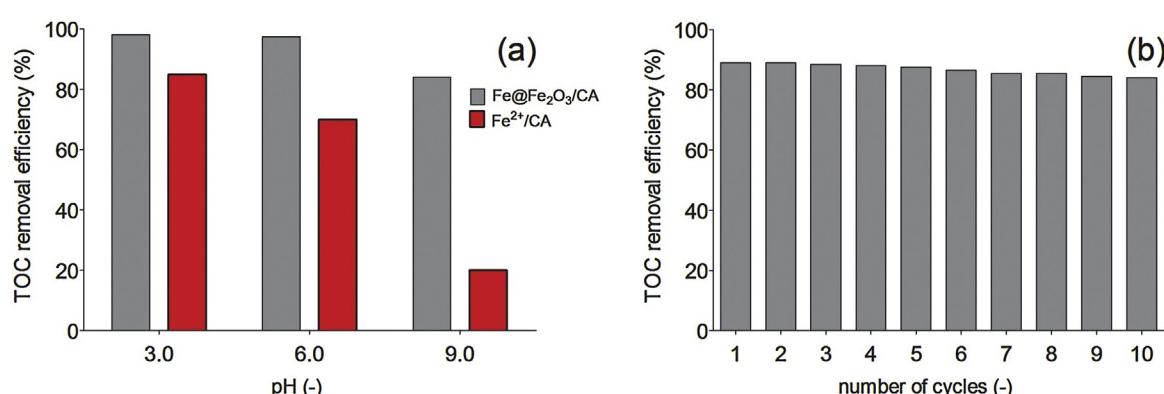

Fig. 14. (a) comparison of TOC removal efficiency at different pH for Fe@Fe_2O_3/CA and CA with $1\,mM\,L^{-1}$ Fe^{2+} during the treatment of 100 mL of $500\,mg\,L^{-1}$ metalaxyl solution in 0.1 M Na_2SO_4 at $10\,mA\,cm^{-2}$ using BDD anode and (b) reusability of Fe@Fe_2O_3/CA during the 4 h a cycle at similar condition as (a). Reprinted with the permission of Ref. [20].

which reduces the effective surface area and active site of the catalyst and in turn the efficiency of the system. This is particularly the case of magnetic Fe-containing nanocatalyst like Fe_3O_4 and Fe° where the nanoparticles not only attached to one another but also very difficult to agitate the electrolytic system, even though such system has an advantage of easy separation of the catalyst for possible reuse. More so, most synthetic supported or non-supported catalyst as well as Fe-functionalized cathode requires either multi-steps or complex preparation techniques which has limited most studies on Hetero-EF system to laboratory or pre-pilot scale. A typical example is functionalized CAs whose preparation involves at least four different non-related steps, thus makes the preparation route a bit complex, even though functionalized CAs remains one the most efficient heterogeneous catalyst/cathode based on literature.

Future studies in Hetero-EF and Hetero-PEF approaches should be tailored towards developing low-cost solid catalyst with improve stability in acidic pH, treatment of real wastewater, scale-up/pilot plant and flow-reactors based on these systems and in-situ spectroscopy studies of the H_2O_2 activation mechanisms at the surface of the solid catalyst. It is important to enhance the stability of the solid catalyst at acidic pH values as studies have shown that most of the existing catalysts undergo significant leaching at strong acidic pH values, which make the system, behave like homogeneous EF and PEF processes. The economic cost and environmental impacts of both existing and future solid catalysts and functionalized cathodic materials should be considered in forthcoming studies. Previous studies on Hetero-EF has failed to address these key issues especially the environmental impact of the nanocatalysts on biotic component of the ecosystem of the receiving water bodies, where wastewaters are disposed after treatment. This information is crucial to engineers and regulatory agencies/bodies in charge of adapting new technologies. Besides, more studies are still required on the application of Hetero-EF for the treatment of real wastewater with complete cost analysis because there is a significant difference in the behavior of real and synthetic wastewater during the electrochemical treatment. Real wastewaters are complex in composition and properties; as such their electrochemical treatment may behave differently in terms of efficiency and removal mechanisms when compared to synthetic wastewater. Both the ·OH scavenging effect of the inorganic ions and natural organic matters in the real wastewater as well as synergistic effect of the different organic pollutants on the efficiency of the Hetero-EF process require further studies.

The mechanisms of activation of H_2O_2 to ·OH have not been extensive studied and no consensus on reactions involved till date in literature. Therefore, more detail investigations are still require to understand the mechanisms and reactions involved in heterogeneous catalytic decomposition of the H_2O_2. *In situ* spectroscopic techniques such as ATR-FTIR, EIS and DFT simulations and microscopy studies about the treated solution may be of good assistance in understanding the mechanisms and reactions involved in H_2O_2 activation as well as those responsible for the transformation of the pollutants, thus allows adequate design of the electrochemical reactors and optimization of operating conditions. More importantly, there is need for pre-pilot, pilot and scale-up studies for Hetero-EF system with both catalysts and functionalized cathode material for treatment of synthetic and real effluents. Till date, all the studies reported in literature was performed on laboratory scale; as such full scale studies are required to understand the behavior of Hetero-EF system on large scale treatment reactors as well as optimization works with full cost and environmental impact. Besides, studies on flow reactors using either solid catalysts or functionalized cathode are very limited in literature, which implies that more studies are need to investigate feasibility of Hetero-EF system in flow reactors with aim of addressing the technical and economic perspectives.

8. Conclusion remarks

Heterogeneous electrochemical wastewater treatment system based on Fenton's chemistry is one of the most exciting and efficient emerging technologies for wastewater treatment owing to its applicability over wide pH widows and reusability of the catalysts in several runs. The desirable features for potential heterogeneous catalysts include high catalytic efficiency and stability over wide pH range, easy separation and reusability as well as environmental compatibility. The catalytic activation of H_2O_2 to reactive oxygen species, especially ·OH, was by either homogeneous catalysis by dissolved M^{x+1}/M^x (M=Fe, Cu or Co) redox couple or surface catalyzed process by surface metal species $\equiv M^x-OH$ (M=Fe, Cu or Co) and its one-electron reduzate ($\equiv M^{x-1}-OH$) or both depending on the working pH at which the system operate and partly on the properties of the solid catalyst. Two known configurations of Hetero-EF and Hetero-PEF systems *vis-à-vis* solid catalysts (bare or supported iron/transition metal containing compounds) and Fe/Fe-compound functionalized cathodic materials were vividly examined. Relevant studies on Hetero-EF and Hetero-PEF approaches by using both solid catalysts and functionalized cathodic materials were summarized and it is safe to say that the latter is a more exciting treatment technique because of easy separation and reusability.

Catalytic fall-off, dissolution at strong acidic pH and agglomeration as well as multi-step/complex techniques for catalyst/functionalized cathode preparation are some of the major challenges encounter in Hetero-EF and Hetero-PEF treatments of organic pollutants. It can be anticipated that more studies and research groups will consider Hetero-systems in future due to it exciting features and logical growth in environmental concern and pollution remediation. Therefore future studies should be focused on improving the stability of the solid catalyst at acidic pH, investigating the use of Hetero-EF/PEF system on pilot scale and flow reactors and complete analysis of the economic and environmental impact of Hetero-EF treatment on biotic component of ecosystem as well as treatment of real wastewater.

Acknowledgements

References

[1] M.A. Oturan, J.J. Aaron, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2577–2641.
[2] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review, Chem. Rev. 115 (2015) 13362–13407.
[3] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev. 109 (2009) 6541–6569.
[4] E. Brillas, I. Sires, M.A. Oturan, Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry, Chem. Rev. 109 (2009) 6570–6631.
[5] S.O. Ganiyu, E.D. van Hullebusch, M. Cretin, G. Esposito, M.A. Oturan, Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: a critical review, Sep. Purif. Technol. 156 (2015) 891–914.
[6] S.O. Ganiyu, N. Oturan, S. Raffy, M. Cretin, R. Esmilaire, E. van Hullebusch, G. Esposito, M.A. Oturan, Sub-stoichiometric titanium oxide (Ti_4O_7) as a suitable

ceramic anode for electrooxidation of organic pollutants: a case study of kinetics, mineralization and toxicity assessment of amoxicillin, Water Res. 106 (2016) 171–182.

[7] I. Sirés, E. Brillas, Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: a review, Environ. Int. 40 (2012) 212–229.

[8] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow. A review, Environ. Sci. Pollut. Res. 21 (2014) 8336–8367.

[9] L. Feng, E.D. van Hullebusch, M.A. Rodrigo, G. Esposito, M.A. Oturan, Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review, Chem. Eng. J. 228 (2013) 944–964.

[10] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters, Appl. Catal. B: Environ. 202 (2017) 217–261.

[11] J. Radjenovic, D.L. Sedlak, Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water, Environ. Sci. Technol. 49 (2015) 11292–11302.

[12] M.A. Oturan, Electrochemical advanced oxidation technologies for removal of organic pollutants from water, Environ. Sci. Pollut. Res. 21 (2014) 8333–8335.

[13] C.A. Martínez-Huitle, E. Brillas, Electrochemical alternatives for drinking water disinfection, Angew. Chem. Int. Ed. 47 (2008) 1998–2005.

[14] E. Brillas, A review on the degradation of organic pollutants in waters by UV photoelectro-Fenton and solar photoelectro-Fenton, J. Braz. Chem. Soc. 25 (2014) 393–417.

[15] S. Vasudevan, M.A. Oturan, Electrochemistry: as cause and cure in water pollution—an overview, Environ. Chem. Lett. 12 (2014) 97–108.

[16] M.A. Rodrigo, N. Oturan, M.A. Oturan, Electrochemically assisted remediation of pesticides in soils and water: a review, Chem. Rev. 114 (2014) 8720–8745.

[17] K.V. Plakas, A.J. Karabelas, Electro-Fenton Applications in the Water Industry, Springer Berlin Heidelberg, Berlin, Heidelberg, 2017.

[18] H. Lin, N. Oturan, J. Wu, M.A. Oturan, H. Zhang, The Application of Electro-Fenton Process for the Treatment of Artificial Sweeteners, Springer Berlin Heidelberg, Berlin, Heidelberg, 2017.

[19] S.O. Ganiyu, T.X. Huong Le, M. Bechelany, G. Esposito, E.D. van Hullebusch, M.A. Oturan, M. Cretin, A hierarchical CoFe-layered double hydroxide modified carbon-felt cathode for heterogeneous electro-Fenton process, J. Mater. Chem. A 5 (2017) 3655–3666.

[20] Y. Wang, G. Zhao, S. Chai, H. Zhao, Y. Wang, Three-dimensional homogeneous ferrite-carbon aerogel: one pot fabrication and enhanced electro-Fenton reactivity, ACS Appl. Mater. Interfaces 5 (2013) 842–852.

[21] J. Li, Z. Ai, L. Zhang, Design of a neutral electro-Fenton system with $Fe@Fe_2O_3$/ACF composite cathode for wastewater treatment, J. Hazard. Mater. 164 (2009) 18–25.

[22] P.V. Nidheesh, H. Olvera-Vargas, N. Oturan, M.A. Oturan, Heterogeneous Electro-Fenton Process: Principles and Applications, Springer Berlin Heidelberg, Berlin, Heidelberg, 2017.

[23] C.M. Sánchez-Sánchez, E. Expósito, J. Casado, V. Montiel, Goethite as a more effective iron dosage source for mineralization of organic pollutants by electro-Fenton process, Electrochem. Commun. 9 (2007) 19–24.

[24] E. Expósito, C.M. Sánchez-Sánchez, V. Montiel, Mineral iron oxides as iron source in electro-Fenton and photoelectro-Fenton mineralization processes, J. Electrochem. Soc. 154 (2007) E116.

[25] L. Labiadh, M.A. Oturan, M. Panizza, N.B. Hamadi, S. Ammar, Complete removal of AHPS synthetic dye from water using new electro-fenton oxidation catalyzed by natural pyrite as heterogeneous catalyst, J. Hazard. Mater. 297 (2015) 34–41.

[26] N. Barhoumi, N. Oturan, H. Olvera-Vargas, E. Brillas, A. Gadri, S. Ammar, M.A. Oturan, Pyrite as a sustainable catalyst in electro-Fenton process for improving oxidation of sulfamethazine. Kinetics, mechanism and toxicity assessment, Water Res. 94 (2016) 52–61.

[27] N. Barhoumi, L. Labiadh, M.A. Oturan, N. Oturan, A. Gadri, S. Ammar, E. Brillas, Electrochemical mineralization of the antibiotic levofloxacin by electro-Fenton-pyrite process, Chemosphere 141 (2015) 250–257.

[28] S. Ammar, M.A. Oturan, L. Labiadh, A. Guersalli, R. Abdelhedi, N. Oturan, E. Brillas, Degradation of tyrosol by a novel electro-Fenton process using pyrite as heterogeneous source of iron catalyst, Water Res. 74 (2015) 77–87.

[29] B. Hou, H. Han, S. Jia, H. Zhuang, P. Xu, D. Wang, Heterogeneous electro-Fenton oxidation of catechol catalyzed by nano-Fe_3O_4: kinetics with the Fermi's equation, J. Taiwan Inst. Chem. Eng. 56 (2015) 138–147.

[30] G. Zhang, Y. Zhou, F. Yang, FeOOH-catalyzed heterogeneous electro-Fenton system upon anthraquinone@graphene nanohybrid cathode in a divided electrolytic cell: catholyte-regulated catalytic oxidation performance and mechanism, J. Electrochem. Soc. 162 (2015) H357–H365.

[31] S.B. Hammouda, F. Fourcade, A. Assadi, I. Soutrel, N. adhoum, A. Amrane, L. Monser, Effective heterogeneous electro-Fenton process for the degradation of a malodorous compound, indole, using iron loaded alginate beads as a reusable catalyst, Appl. Catal. B Environ. 182 (2016) 47–58.

[32] W. Chen, X. Yang, J. Huang, Y. Zhu, Y. Zhou, Y. Yao, C. Li, Iron oxide containing graphene/carbon nanotube based carbon aerogel as an efficient E-Fenton cathode for the degradation of methyl blue, Electrochim. Acta 200 (2016) 75–83.

[33] S.D. Sklari, K.V. Plakas, P.N. Petsi, V.T. Zaspalis, A.J. Karabelas, Toward the development of a novel electro-Fenton system for eliminating toxic organic substances from water. Part 2. Preparation, characterization, and evaluation of iron-impregnated carbon felts as cathodic electrodes, Ind. Eng. Chem. Res. 54 (2015) 2059–2073.

[34] F.A. Nasr, H.S. Doma, H.S. Abdel-Halim, S.A. El-Shafai, Chemical industry wastewater treatment, J. Eng. Appl. Sci.-CAIRO 52 (2005) 697.

[35] L. Bilińska, M. Gmurek, S. Ledakowicz, Comparison between industrial and simulated textile wastewater treatment by AOPs – biodegradability, toxicity and cost assessment, Chem. Eng. J. 306 (2016) 550–559.

[36] C.R. Holkar, A.J. Jadhav, D.V. Pinjari, N.M. Mahamuni, A.B. Pandit, A critical review on textile wastewater treatments: possible approaches, J. Environ. Manage. 182 (2016) 351–366.

[37] W.J. Sim, J.W. Lee, E.S. Lee, S.K. Shin, S.R. Hwang, J.E. Oh, Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures, Chemosphere 82 (2011) 179–186.

[38] A. Fiorentino, A. Gentili, M. Isidori, M. Lavorgna, A. Parrella, F. Temussi, Olive oil mill wastewater treatment using a chemical and biological approach, J. Agric. Food Chem. 52 (2004) 5151–5154.

[39] S. Verma, B. Prasad, I.M. Mishra, Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics, J. Hazard. Mater. 178 (2010) 1055–1064.

[40] S. Zhang, J. Zhang, W. Wang, F. Li, X. Cheng, Removal of phosphate from landscape water using an electrocoagulation process powered directly by photovoltaic solar modules, Sol. Energy Mater. Sol. Cells 117 (2013) 73–80.

[41] L. Zhuang, S. Zhou, Y. Yuan, M. Liu, Y. Wang, A novel bioelectro-Fenton system for coupling anodic COD removal with cathodic dye degradation, Chem. Eng. J. 163 (2010) 160–163.

[42] R. Davarnejad, J. Azizi, Alcoholic wastewater treatment using electro-Fenton technique modified by Fe_2O_3 nanoparticles, J. Environ. Chem. Eng. 4 (2016) 2342–2349.

[43] D. Valero, V. García-García, E. Expósito, A. Aldaz, V. Montiel, Electrochemical treatment of wastewater from almond industry using DSA-type anodes: direct connection to a PV generator, Sep. Purif. Technol. 123 (2014) 15–22.

[44] M. Zhou, L. Liu, Y. Jiao, Q. Wang, Q. Tan, Treatment of high-salinity reverse osmosis concentrate by electrochemical oxidation on BDD and DSA electrodes, Desalination 277 (2011) 201–206.

[45] H. Zhou, Y. Wang, Y. Wang, T. Cao, G. Zhao, Electro-Fenton oxidation of pesticides with a novel $Fe_3O_4@Fe_2O_3$/activated carbon aerogel cathode: high activity, wide pH range and catalytic mechanism, Appl. Catal. B Environ. 125 (2012) 120–127.

[46] L. Liang, Y. An, M. Zhou, F. Yu, M. Liu, G. Ren, Novel rolling-made gas-diffusion electrode loading trace transition metal for efficient heterogeneous electro-Fenton-like, J. Environ. Chem. Eng. 4 (2016) 4400–4408.

[47] W.P. Kwan, B.M. Voelker, Decomposition of hydrogen peroxide and organic compounds in the presence of dissolved iron and ferrihydrate, Environ. Sci. Technol. 36 (2002) 1467–1476.

[48] A.L.T. Pham, C. Lee, F.M. Doyle, D.L. Sedlak, A silica-supported iron oxide catalyst capable of activating hydrogen peroxide at neutral pH values, Environ. Sci. Technol. 43 (2009) 8930–8935.

[49] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B Environ. 47 (2004) 219–256.

[50] Y. Huang, C. Han, Y. Liu, M.N. Nadagouda, L. Machala, K.E. O'Shea, V.K. Sharma, D.D. Dionysiou, Degradation of atrazine by $Zn_xCu_{1−x}Fe_2O_4$ nanomaterial-catalyzed sulfite under UV–vis light irradiation: Green strategy to generate $SO_4{}^−$, Appl. Catal. B Environ. 221 (2018) 380–392.

[51] W.F. de Souza, I.R. Guimarães, L.C.A. Oliveira, A.S. Giroto, M.C. Guerreiro, C.L.T. Silva, Effect of Ni incorporation into goethite in the catalytic activity for the oxidation of nitrogen compounds in petroleum, Appl. Catal. Gen. 381 (2010) 36–41.

[52] R. Costa, M. Lelis, L. Oliveira, J. Fabris, J. Ardisson, R. Rios, C. Silva, R. Lago, Novel active heterogeneous Fenton system based on $Fe_{3−x}M_xO_4$ (Fe, Co, Mn, Ni): the role of M^{2+} species on the reactivity towards H_2O_2 reactions, J. Hazard. Mater. 129 (2006) 171–178.

[53] R.C.C. Costa, M. de F.F. Lelis, L.C.A. Oliveira, J.D. Fabris, J.D. Ardisson, R.R.V.A. Rios, C.N. Silva, R.M. Lago, Remarkable effect of Co and Mn on the activity of $Fe_{3−x}M_xO4$ promoted oxidation of organic contaminants in aqueous medium with H_2O_2, Catal. Commun. 4 (2003) 525–529.

[54] Y. Zhong, X. Liang, W. Tan, Y. Zhong, H. He, J. Zhu, P. Yuan, Z. Jiang, A comparative study about the effects of isomorphous substitution of transition metals (Ti, Cr, Mn, Co and Ni) on the UV/Fenton catalytic activity of magnetite, J. Mol. Catal. Chem. 372 (2013) 29–34.

[55] X. Liang, Y. Zhong, S. Zhu, L. Ma, P. Yuan, J. Zhu, H. He, Z. Jiang, The contribution of vanadium and titanium on improving methylene blue decolorization through heterogeneous UV-Fenton reaction catalyzed by their co-doped magnetite, J. Hazard. Mater. 199–200 (2012) 247–254.

[56] X. Liang, S. Zhu, Y. Zhong, J. Zhu, P. Yuan, H. He, J. Zhang, The remarkable effect of vanadium doping on the adsorption and catalytic activity of magnetite in the decolorization of methylene blue, Appl. Catal. B Environ. 97 (2010) 151–159.

[57] F. Magalhães, M.C. Pereira, S.E.C. Botrel, J.D. Fabris, W.A. Macedo, R. Mendonça, R.M. Lago, L.C.A. Oliveira, Cr-containing magnetites $Fe_{3−x}Cr_xO_4$: the role of Cr^{3+} and Fe^{2+} on the stability and reactivity towards H_2O_2 reactions, Appl. Catal. Gen. 332 (2007) 115–123.

[58] J. Shi, Z. Ai, L. Zhang, $Fe@Fe_2O_3$ core-shell nanowires enhanced Fenton oxidation by accelerating the Fe(III)/Fe(II) cycles, Water Res. 59 (2014) 145–153.

[59] L. Guo, F. Chen, X. Fan, W. Cai, J. Zhang, S-doped α-Fe_2O_3 as a highly active heterogeneous Fenton-like catalyst towards the degradation of acid orange 7 and phenol, Appl. Catal. B Environ. 96 (2010) 162–168.

[60] N. Barhoumi, H. Olvera-Vargas, N. Oturan, D. Huguenot, A. Gadri, S. Ammar, E. Brillas, M.A. Oturan, Kinetics of oxidative degradation/mineralization pathways of the antibiotic tetracycline by the novel heterogeneous electro-Fenton process

with solid catalyst chalcopyrite, Appl. Catal. B Environ. 209 (2017) 637–647.

[61] G.B. Ortiz de la Plata, O.M. Alfano, A.E. Cassano, Decomposition of 2-chlor-ophenol employing goethite as Fenton catalyst II: reaction kinetics of the het-erogeneous Fenton and photo-Fenton mechanisms, Appl. Catal. B Environ. 95 (2010) 14–25.

[62] G.B. Ortiz de la Plata, O.M. Alfano, A.E. Cassano, Decomposition of 2-chlor-ophenol employing goethite as Fenton catalyst. I. Proposal of a feasible, combined reaction scheme of heterogeneous and homogeneous reactions, Appl. Catal. B Environ. 95 (2010) 1–13.

[63] Z. Ai, T. Mei, J. Liu, J. Li, F. Jia, L. Zhang, J. Qiu, Fe@Fe₂O₃ core − shell nanowires as an iron reagent. 3. Their combination with CNTs as an effective oxygen-fed gas diffusion electrode in a neutral electro-Fenton system, J. Phys. Chem. C 111 (2007) 14799–14803.

[64] W. Liu, Z. Ai, M. Cao, L. Zhang, Ferrous ions promoted aerobic simazine de-gradation with Fe@Fe₂O₃ core–shell nanowires, Appl. Catal. B Environ. 150–151 (2014) 1–11.

[65] Q. Huang, M. Cao, Z. Ai, L. Zhang, Reactive oxygen species dependent degradation pathway of 4-chlorophenol with Fe@Fe₂O₃ core–shell nanowires, Appl. Catal. B Environ. 162 (2015) 319–326.

[66] R. Gonzalez-Olmos, M.J. Martin, A. Georgi, F.D. Kopinke, I. Oller, S. Malato, Fe-zeolites as heterogeneous catalysts in solar Fenton-like reactions at neutral pH, Appl. Catal. B Environ. 125 (2012) 51–58.

[67] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, Degradation of azo-dye orange II by a photoassisted Fenton reaction using a novel composite of iron oxide and silicate nanoparticles as a catalyst, Ind. Eng. Chem. Res. 42 (2003) 2058–2066.

[68] M. Pariente, F. Martinez, J. Melero, J. Botas, T. Velegraki, N. Xekoukoulotakis, D. Mantzavinos, Heterogeneous photo-Fenton oxidation of benzoic acid in water: effect of operating conditions, reaction by-products and coupling with biological treatment, Appl. Catal. B Environ. 85 (2008) 24–32.

[69] M. Luo, D. Bowden, P. Brimblecombe, Catalytic property of Fe-Al pillared clay for Fenton oxidation of phenol by H₂O₂, Appl. Catal. B Environ. 85 (2009) 201–206.

[70] W. Najjar, S. Azabou, S. Sayadi, A. Ghorbel, Screening of Fe–BEA catalysts for wet hydrogen peroxide oxidation of crude olive mill wastewater under mild condi-tions, Appl. Catal. B Environ. 88 (2009) 299–304.

[71] J.A. Bañuelos, F.J. Rodríguez, J. Manríquez Rocha, E. Bustos, A. Rodríguez, J.C. Cruz, L.G. Arriaga, L.A. Godínez, Novel electro-Fenton approach for re-generation of activated carbon, Environ. Sci. Technol. 47 (2013) 7927–7933.

[72] A. Cruz, L. Couto, S. Esplugas, C. Sans, Study of the contribution of homogeneous catalysis on heterogeneous Fe(III)/alginate mediated photo-Fenton process, Chem. Eng. J. 318 (2017) 272–280.

[73] O. García-Rodríguez, J.A. Bañuelos, L.A. Godínez, H.C. Arredondo Valdez, E. Zamudio, V. Ramírez, F.J. Rodríguez-Valadez, Iron supported on ion exchange resin as source of iron for Fenton reagent: a heterogeneous or a homogeneous Fenton reagent generation? Int. J. Chem. React. Eng. 15 (2017) 1–11.

[74] M. Cheng, W. Ma, J. Li, Y. Huang, J. Zhao, Y. xiang Wen, Y. Xu, Visible-light-assisted degradation of dye pollutants over Fe(III)-loaded resin in the presence of H₂O₂ at neutral pH values, Environ. Sci. Technol. 38 (2004) 1569–1575.

[75] A. El-Ghenymy, N. Oturan, M.A. Oturan, J.A. Garrido, P.L. Cabot, F. Centellas, R.M. Rodríguez, E. Brillas, Comparative electro-Fenton and UVA photoelectro-Fenton degradation of the antibiotic sulfanilamide using a stirred BDD/air-diffu-sion tank reactor, Chem. Eng. J. 234 (2013) 115–123.

[76] M.A. Oturan, J. Peiroten, P. Chartrin, A.J. Acher, Complete destruction of *p*-ni-trophenol in aqueous medium by electro-Fenton method, Environ. Sci. Technol. 34 (2000) 3474–3479.

[77] T.X.H. Le, M. Bechelany, S. Lacour, N. Oturan, M.A. Oturan, M. Cretin, High re-moval efficiency of dye pollutants by electron-Fenton process using a graphene based cathode, Carbon 94 (2015) 1003–1011.

[78] N. Oturan, S.O. Ganiyu, S. Raffy, M.A. Oturan, Sub-stoichiometric titanium oxide as a new anode material for electro-Fenton process: application to electrocatalytic destruction of antibiotic amoxicillin, Appl. Catal. B Environ. 217 (2017) 214–223.

[79] T.X. Huong Le, M. Bechelany, M. Cretin, Carbon felt based-electrodes for energy and environmental applications: a review, Carbon 122 (2017) 564–591.

[80] N. Qiao, H. Ma, M. Hu, Design of a neutral three-dimensional electro-Fenton system with various bentonite-based Fe particle electrodes: a comparative study, Mater. Res. Innov. 19 (2015) S2-137-S2-141.

[81] E.G. Garrido-Ramírez, M.L. Mora, J.F. Marco, M.S. Ureta-Zañartu, Characterization of nanostructured allophane clays and their use as support of iron species in a heterogeneous electro-Fenton system, Appl. Clay Sci. 86 (2013) 153–161.

[82] E.G. Garrido-Ramírez, J.F. Marco, N. Escalona, M.S. Ureta-Zañartu, Preparation and characterization of bimetallic Fe–Cu allophane nanoclays and their activity in the phenol oxidation by heterogeneous electro-Fenton reaction, Microporous Mesoporous Mater. 225 (2016) 303–311.

[83] M.D.G. de Luna, M.L. Veciana, C.C. Su, M.-C. Lu, Acetaminophen degradation by electro-Fenton and photoelectro-Fenton using a double cathode electrochemical cell, J. Hazard. Mater. 217–218 (2012) 200–207.

[84] H. Zhao, Y. Chen, Q. Peng, Q. Wang, G. Zhao, Catalytic activity of MOF(2Fe/Co)/carbon aerogel for improving H₂O₂ and OH generation in solar photo–electro–Fenton process, Appl. Catal. B Environ. 203 (2017) 127–137.

[85] A.L.T. Pham, F.M. Doyle, D.L. Sedlak, Inhibitory effect of dissolved silica on H₂O₂ decomposition by iron(III) and manganese(IV) oxides: implications for H₂O₂-based in situ chemical oxidation, Environ. Sci. Technol. 46 (2012) 1055–1062.

[86] A. Stefánsson, Iron(III) hydrolysis and solubility at 25 °C, Environ. Sci. Technol. 41 (2007) 6117–6123.

[87] W.P. Kwan, B.M. Voelker, Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems, Environ. Sci.

Technol. 37 (2003) 1150–1158.

[88] B.R. Petigara, N.V. Blough, A.C. Mignerey, Mechanisms of hydrogen peroxide decomposition in soils, Environ. Sci. Technol. 36 (2002) 639–645.

[89] F. Moura, G. Oliveira, M. Araujo, J. Ardisson, W. Macedo, R. Lago, Highly reactive species formed by interface reaction between Fe°–iron oxides particles: an efficient electron transfer system for environmental applications, Appl. Catal. Gen. 307 (2006) 195–204.

[90] L. Hou, Q. Zhang, F. Jérôme, D. Duprez, H. Zhang, S. Royer, Shape-controlled nanostructured magnetite-type materials as highly efficient Fenton catalysts, Appl. Catal. B Environ. 144 (2014) 739–749.

[91] M. Munoz, Z.M. de Pedro, J.A. Casas, J.J. Rodriguez, Preparation of magnetite-based catalysts and their application in heterogeneous Fenton oxidation—a re-view, Appl. Catal. B Environ. 176–177 (2015) 249–265.

[92] Y. Wang, H. Zhao, S. Chai, Y. Wang, G. Zhao, D. Li, Electrosorption enhanced electro-Fenton process for efficient mineralization of imidacloprid based on mixed-valence iron oxide composite cathode at neutral pH, Chem. Eng. J. 223 (2013) 524–535.

[93] X. Hu, B. Liu, Y. Deng, H. Chen, S. Luo, C. Sun, P. Yang, S. Yang, Adsorption and heterogeneous Fenton degradation of 17α-methyltestosterone on nano Fe₃O₄/MWCNTs in aqueous solution, Appl. Catal. B Environ. 107 (2011) 274–283.

[94] S. Chou, C. Huang, Y.H. Huang, Heterogeneous and homogeneous catalytic oxi-dation by supported γ-FeOOH in a fluidized-bed reactor: kinetic approach, Environ. Sci. Technol. 35 (2001) 1247–1251.

[95] S. Chou, C. Huang, Application of a supported iron oxyhydroxide catalyst in oxi-dation of benzoic acid by hydrogen peroxide, Chemosphere 38 (1999) 2719–2731.

[96] W.R.P. Barros, J.R. Steter, M.R.V. Lanza, A.C. Tavares, Catalytic activity of Fe₃₋ₓCuₓO₄ (0 ≤ x ≤ 0.25) nanoparticles for the degradation of Amaranth food dye by heterogeneous electro-Fenton process, Appl. Catal. B Environ. 180 (2016) 434–441.

[97] H. Zhao, L. Qian, X. Guan, D. Wu, G. Zhao, Continuous bulk FeCuC aerogel with ultradispersed metal nanoparticles: an efficient 3D heterogeneous electro-Fenton cathode over a wide range of pH 3–9, Environ. Sci. Technol. 50 (2016) 5225–5233.

[98] R. Salazar, E. Brillas, I. Sirés, Finding the best Fe²⁺/Cu²⁺ combination for the solar photoelectro-Fenton treatment of simulated wastewater containing the in-dustrial textile dye disperse blue 3, Appl. Catal. B Environ. 115–116 (2012) 107–116.

[99] I. Sirés, J.A. Garrido, R.M. Rodríguez, P.L. Cabot, F. Centellas, C. Arias, E. Brillas, Electrochemical degradation of paracetamol from water by catalytic action of Fe²⁺, Cu²⁺, and UVA light on electrogenerated hydrogen peroxide, J. Electrochem. Soc. 153 (2006) D1.

[100] M. Pimentel, N. Oturan, M. Dezotti, M.A. Oturan, Phenol degradation by advanced electrochemical oxidation process electro-Fenton using a carbon felt cathode, Appl. Catal. B Environ. 83 (2008) 140–149.

[101] E. do Vale-Júnior, S. Dosta, I.G. Cano, J.M. Guilemany, S. Garcia-Segura, C.A. Martínez-Huitle, Acid blue 29 decolorization and mineralization by anodic oxidation with a cold gas spray synthesized Sn–Cu–Sb alloy anode, Chemosphere 148 (2016) 47–54.

[102] R.C.C. Costa, F.C.C. Moura, J.D. Ardisson, J.D. Fabris, R.M. Lago, Highly active heterogeneous Fenton-like systems based on Fe°/Fe₃O₄ composites prepared by controlled reduction of iron oxides, Appl. Catal. B Environ. 83 (2008) 131–139.

[103] J.E. Amonette, D.J. Workman, D.W. Kennedy, J.S. Fruchter, Y.A. Gorby, Dechlorination of carbon tetrachloride by Fe(II) associated with goethite, Environ. Sci. Technol. 34 (2000) 4606–4613.

[104] S. Navalon, M. Alvaro, H. Garcia, Heterogeneous Fenton catalysts based on clays, silicas and zeolites, Appl. Catal. B Environ. 99 (2010) 1–26.

[105] J. Herney-Ramirez, M. Lampinen, M.A. Vicente, C.A. Costa, L.M. Madeira, Experimental design to optimize the oxidation of orange II dye solution using a clay-based Fenton-like catalyst, Ind. Eng. Chem. Res. 47 (2008) 284–294.

[106] J. Herney-Ramirez, M.A. Vicente, L.M. Madeira, Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: a review, Appl. Catal. B Environ. 98 (2010) 10–26.

[107] N. Banić, B. Abramović, J. Krstić, D. Šojić, D. Lončarević, Z. Cherkezova-Zheleva, V. Guzsvány, Photodegradation of thiacloprid using Fe/TiO₂ as a heterogeneous photo-Fenton catalyst, Appl. Catal. B Environ. 107 (2011) 363–371.

[108] I. Sirés, J.A. Garrido, R.M. Rodríguez, E. Brillas, N. Oturan, M.A. Oturan, Catalytic behavior of the Fe³⁺/Fe²⁺ system in the electro-Fenton degradation of the anti-microbial chlorophene, Appl. Catal. B Environ. 72 (2007) 382–394.

[109] J. Feng, X. Hu, P.L. Yue, Discoloration and mineralization of orange II using dif-ferent heterogeneous catalysts containing Fe: a comparative study, Environ. Sci. Technol. 38 (2004) 5773–5778.

[110] J. Feng, X. Hu, P.L. Yue, Novel bentonite clay-based Fe − nanocomposite as a heterogeneous catalyst for photo-Fenton discoloration and mineralization of or-ange II, Environ. Sci. Technol. 38 (2004) 269–275.

[111] K.V. Plakas, A.J. Karabelas, S.D. Sklari, V.T. Zaspalis, Toward the development of a novel electro-Fenton system for eliminating toxic organic substances from water. Part 1. In situ generation of hydrogen peroxide, Ind. Eng. Chem. Res. 52 (2013) 13948–13956.

[112] J.A. Banuelos, O. Garcia-Rodriguez, F.J. Rodriguez-Valadez, L.A. Godinez, Electrochemically prepared iron-modified activated carbon electrodes for their application in electro-Fenton and photoelectro-Fenton processes, J. Electrochem. Soc. 162 (2015) E154–E159.

[113] A.C. Silva, R.M. Cepera, M.C. Pereira, D.Q. Lima, J.D. Fabris, L.C.A. Oliveira, Heterogeneous catalyst based on peroxo-niobium complexes immobilized over iron oxide for organic oxidation in water, Appl. Catal. B Environ. 107 (2011) 237–244.

[114] A.C. Silva, D.Q.L. Oliveira, L.C.A. Oliveira, A.S. Anastácio, T.C. Ramalho, J.H. Lopes, H.W.P. Carvalho, C.E.R. Torres, Nb-containing hematites $Fe_{2-x}Nb_xO_3$: the role of Nb^{5+} on the reactivity in presence of the H_2O_2 or ultraviolet light, Appl. Catal. Gen. 357 (2009) 79–84.

[115] Q. Wang, S. Tian, J. Long, P. Ning, Use of Fe(II)Fe(III)-LDHs prepared by co-precipitation method in a heterogeneous-Fenton process for degradation of methylene blue, Catal. Today 224 (2014) 41–48.

[116] L. Liang, F. Yu, Y. An, M. Liu, M. Zhou, Preparation of transition metal composite graphite felt cathode for efficient heterogeneous electro-Fenton process, Environ. Sci. Pollut. Res. 24 (2017) 1122–1132.

[117] O. Iglesias, M.A.F. de Dios, T. Tavares, M.A. Sanromán, M. Pazos, Heterogeneous electro-Fenton treatment: preparation, characterization and performance in groundwater pesticide removal, J. Ind. Eng. Chem. 27 (2015) 276–282.

[118] N. Barhoumi, N. Oturan, S. Ammar, A. Gadri, M.A. Oturan, E. Brillas, Enhanced degradation of the antibiotic tetracycline by heterogeneous electro-Fenton with pyrite catalysis, Environ. Chem. Lett. 15 (2017) 689–693.

[119] I. Ouiriemmi, A. Karrab, N. Oturan, M. Pazos, E. Rozales, A. Gadri, M.Á. Sanromán, S. Ammar, M.A. Oturan, Heterogeneous electro-Fenton using natural pyrite as solid catalyst for oxidative degradation of vanillic acid, J. Electroanal. Chem. 797 (2017) 69–77.

[120] A.V.B. Reddy, Z. Yusop, J. Jaafar, Y.V.M. Reddy, A.B. Aris, Z.A. Majid, J. Talib, G. Madhavi, Recent progress on Fe-based nanoparticles: synthesis, properties, characterization and environmental applications, J. Environ. Chem. Eng. 4 (2016) 3537–3553.

[121] D. Xu, X. Song, W. Qi, H. Wang, Z. Bian, Degradation mechanism, kinetics, and toxicity investigation of 4-bromophenol by electrochemical reduction and oxidation with Pd–Fe/graphene catalytic cathodes, Chem. Eng. J. 333 (2018) 477–485.

[122] B. Huang, C. Qi, Z. Yang, Q. Guo, W. Chen, G. Zeng, C. Lei, Pd/Fe_3O_4 nanocatalysts for highly effective and simultaneous removal of humic acids and Cr(VI) by electro-Fenton with H_2O_2 in situ electro-generated on the catalyst surface, J. Catal. 352 (2017) 337–350.

[123] M. Luo, S. Yuan, M. Tong, P. Liao, W. Xie, X. Xu, An integrated catalyst of Pd supported on magnetic Fe_3O_4 nanoparticles: simultaneous production of H_2O_2 and Fe^{2+} for efficient electro-Fenton degradation of organic contaminants, Water Res. 48 (2014) 190–199.

[124] K. Kim, P. Qiu, M. Cui, J. Khim, Development and application of Fe_3O_4–Pd nanospheres as catalyst for electrochemical-heterogeneous Fenton process, Chem. Eng. J. 284 (2016) 1165–1173.

[125] P. Liao, S. Yuan, M. Chen, M. Tong, W. Xie, P. Zhang, Regulation of electrochemically generated ferrous ions from an iron cathode for Pd-catalytic transformation of MTBE in groundwater, Environ. Sci. Technol. 47 (2013) 7918–7926.

[126] S. Yuan, Y. Fan, Y. Zhang, M. Tong, P. Liao, Pd-catalytic in situ generation of H_2O_2 from H_2 and O_2 produced by water electrolysis for the efficient electro-Fenton degradation of rhodamine B, Environ. Sci. Technol. 45 (2011) 8514–8520.

[127] S. Yuan, X. Mao, A.N. Alshawabkeh, Efficient degradation of TCE in groundwater using Pd and electro-generated H_2 and O_2: a shift in pathway from hydro-dechlorination to oxidation in the presence of ferrous ions, Environ. Sci. Technol. 46 (2012) 3398–3405.

[128] Q. Shi, H. Wang, S. Liu, L. Pang, Z. Bian, Electrocatalytic reduction-oxidation of chlorinated phenols using a nanostructured Pd-Fe modified graphene catalyst, Electrochim. Acta 178 (2015) 92–100.

[129] C. Luo, Z. Chen, D. Wu, L. Ma, Electrochemical reductive degradation of chlorobenzene using galvanically replaced Pd/Fe nanoscale particles, Chem. Eng. J. 241 (2014) 376–383.

[130] H. Wang, Z.Y. Bian, D.Z. Sun, Degradation mechanism of 4-chlorophenol with electrogenerated hydrogen peroxide on a Pd/C gas-diffusion electrode, Water Sci. Technol. 63 (2011) 484.

[131] L. Yue, K. Wang, J. Guo, J. Yang, X. Luo, J. Lian, L. Wang, Enhanced electrochemical oxidation of dye wastewater with Fe_2O_3 supported catalyst, J. Ind. Eng. Chem. 20 (2014) 725–731.

[132] A. Özcan, A. Atılır Özcan, Y. Demirci, E. Şener, Preparation of Fe_2O_3 modified kaolin and application in heterogeneous electro-catalytic oxidation of enoxacin, Appl. Catal. B Environ. 200 (2017) 361–371.

[133] J. Wu, W. Pu, C. Yang, M. Zhang, J. Zhang, Removal of benzotriazole by heterogeneous photoelectro-Fenton like process using $ZnFe_2O_4$ nanoparticles as catalyst, J. Environ. Sci. 25 (2013) 801–807.

[134] L. Gu, F.Y. Song, N.W. Zhu, An innovative electrochemical degradation of 1-diazo-2-naphthol-4-sulfonic acid in the presence of $Bi_2Fe_4O_9$, Appl. Catal. B Environ. 110 (2011) 186–194.

[135] C. Zhang, M. Zhou, X. Yu, L. Ma, F. Yu, Modified iron-carbon as heterogeneous electro-Fenton catalyst for organic pollutant degradation in near neutral pH condition: characterization, degradation activity and stability, Electrochim. Acta 160 (2015) 254–262.

[136] C. Zhang, M. Zhou, G. Ren, X. Yu, L. Ma, J. Yang, F. Yu, Heterogeneous electro-Fenton using modified iron–carbon as catalyst for 2,4-dichlorophenol degradation: influence factors, mechanism and degradation pathway, Water Res. 70 (2015) 414–424.

[137] L. Zhou, Z. Hu, C. Zhang, Z. Bi, T. Jin, M. Zhou, Electrogeneration of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode, Sep. Purif. Technol. 111 (2013) 131–136.

[138] J. Ramírez, L.A. Godínez, M. Méndez, Y. Meas, F.J. Rodríguez, Heterogeneous photo-electro-Fenton process using different iron supporting materials, J. Appl. Electrochem. 40 (2010) 1729–1736.

[139] H.C. Tao, X.Y. Wei, L.J. Zhang, T. Lei, N. Xu, Degradation of p-nitrophenol in a BES-Fenton system based on limonite, J. Hazard. Mater. 254–255 (2013) 236–241.

[140] C.-H. Feng, F.-B. Li, H.-J. Mai, X.-Z. Li, Bio-electro-Fenton process driven by

[141] N. Xu, S. Zhou, Y. Yuan, H. Qin, Y. Zheng, C. Shu, Coupling of anodic biooxidation and cathodic bioelectro-Fenton for enhanced swine wastewater treatment, Bioresour. Technol. 102 (2011) 7777–7783.

[142] H. Wang, H. Luo, P.H. Fallgren, S. Jin, Z.J. Ren, Bioelectrochemical system platform for sustainable environmental remediation and energy generation, Biotechnol. Adv. 33 (2015) 317–334.

[143] H. Wang, Z.J. Ren, A comprehensive review of microbial electrochemical systems as a platform technology, Biotechnol. Adv. 31 (2013) 1796–1807.

[144] K. Solanki, S. Subramanian, S. Basu, Microbial fuel cells for azo dye treatment with electricity generation: a review, Bioresour. Technol. 131 (2013) 564–571.

[145] A. Escapa, R. Mateos, E.J. Martínez, J. Blanes, Microbial electrolysis cells: an emerging technology for wastewater treatment and energy recovery. From laboratory to pilot plant and beyond, Renew. Sustain. Energy Rev. 55 (2016) 942–956.

[146] S. Venkata Mohan, G. Velvizhi, J. Annie Modestra, S. Srikanth, Microbial fuel cell: critical factors regulating bio-catalyzed electrochemical process and recent advancements, Renew. Sustain. Energy Rev. 40 (2014) 779–797.

[147] L. Fu, S.J. You, G. Zhang, F.-L. Yang, X. Fang, Degradation of azo dyes using in-situ Fenton reaction incorporated into H_2O_2-producing microbial fuel cell, Chem. Eng. J. 160 (2010) 164–169.

[148] X. Li, X. Jin, N. Zhao, I. Angelidaki, Y. Zhang, Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell, Bioresour. Technol. 228 (2017) 322–329.

[149] L. Zhang, X. Yin, S.F.Y. Li, Bio-electrochemical degradation of paracetamol in a microbial fuel cell-Fenton system, Chem. Eng. J. 276 (2015) 185–192.

[150] N. Kishimoto, T. Kitamura, M. Kato, H. Otsu, Reusability of iron sludge as an iron source for the electrochemical Fenton-type process using Fe^{2+}/HOCl system, Water Res. 47 (2013) 1919–1927.

[151] E. Rosales, O. Iglesias, M. Pazos, M.A. Sanromán, Decolourisation of dyes under electro-Fenton process using Fe alginate gel beads, J. Hazard. Mater. 213–214 (2012) 369–377.

[152] O. Iglesias, E. Rosales, M. Pazos, M.A. Sanromán, Electro-Fenton decolourisation of dyes in an airlift continuous reactor using iron alginate beads, Environ. Sci. Pollut. Res. 20 (2013) 2252–2261.

[153] O. Iglesias, J. Gómez, M. Pazos, M.Á. Sanromán, Electro-Fenton oxidation of imidacloprid by Fe alginate gel beads, Appl. Catal. B Environ. 144 (2014) 416–424.

[154] O. Iglesias, M.A. Fernández de Dios, E. Rosales, M. Pazos, M.A. Sanromán, Optimisation of decolourisation and degradation of reactive black 5 dye under electro-Fenton process using Fe alginate gel beads, Environ. Sci. Pollut. Res. 20 (2013) 2172–2183.

[155] M.Á. Fernández de Dios, E. Rosales, M. Fernández-Fernández, M. Pazos, M.Á. Sanromán, Degradation of organic pollutants by heterogeneous electro-Fenton process using Mn-alginate composite: Mn-alginate composite as catalyst in electro-Fenton process, J. Chem. Technol. Biotechnol. 90 (2015) 1439–1447.

[156] O. Iglesias, J. Meijide, E. Bocos, M.Á. Sanromán, M. Pazos, New approaches on heterogeneous electro-Fenton treatment of winery wastewater, Electrochimica Acta. 169 (2015) 134–141.

[157] O. Iglesias, M.A. Fernández de Dios, M. Pazos, M.A. Sanromán, Using iron-loaded sepiolite obtained by adsorption as a catalyst in the electro-Fenton oxidation of reactive black 5, Environ. Sci. Pollut. Res. 20 (2013) 5983–5993.

[158] O. Iglesias, M.A.F. de Dios, T. Tavares, M.A. Sanromán, M. Pazos, Heterogeneous electro-Fenton treatment: preparation, characterization and performance in groundwater pesticide removal, J. Ind. Eng. Chem. 27 (2015) 276–282.

[159] Z. He, C. Gao, M. Qian, Y. Shi, J. Chen, S. Song, Electro-Fenton process catalyzed by Fe_3O_4 magnetic nanoparticles for degradation of C.I. Reactive blue 19 in aqueous solution: operating conditions, influence, and mechanism, Ind. Eng. Chem. Res. 53 (2014) 3435–3447.

[160] X. Zeng, K. Hanna, A.T. Lemley, Cathodic Fenton degradation of 4,6-dinitro-o-cresol with nano-magnetite, J. Mol. Catal. Chem. 339 (2011) 1–7.

[161] L. Bounab, O. Iglesias, E. González-Romero, M. Pazos, M. Ángeles Sanromán, Effective heterogeneous electro-Fenton process of m-cresol with iron loaded actived carbon, RSC Adv. 5 (2015) 31049–31056.

[162] Y. Cong, Z. Li, Y. Zhang, Q. Wang, Q. Xu, Synthesis of α-Fe_2O_3/TiO_2 nanotube arrays for photoelectro-Fenton degradation of phenol, Chem. Eng. J. 191 (2012) 356–363.

[163] G. Zhang, S. Wang, S. Zhao, L. Fu, G. Chen, F. Yang, Oxidative degradation of azo dye by hydrogen peroxide electrogenerated in situ on anthraquinonemonosulphonate/polypyrrole composite cathode with heterogeneous CuO/γ-Al_2O_3 catalyst, Appl. Catal. B Environ. 106 (2011) 370–378.

[164] X. Zhu, J. Ni, Simultaneous processes of electricity generation and p-nitrophenol degradation in a microbial fuel cell, Electrochem. Commun. 11 (2009) 274–277.

[165] Y. Luo, R. Zhang, G. Liu, J. Li, B. Qin, M. Li, S. Chen, Simultaneous degradation of refractory contaminants in both the anode and cathode chambers of the microbial fuel cell, Bioresour. Technol. 102 (2011) 3827–3832.

[166] C. Feng, F. Li, H. Liu, X. Lang, S. Fan, A dual-chamber microbial fuel cell with conductive film-modified anode and cathode and its application for the neutral electro-Fenton process, Electrochimica Acta. 55 (2010) 2048–2054.

[167] Z. Es'haghzade, E. Pajootan, H. Bahrami, M. Arami, Facile synthesis of Fe_3O_4 nanoparticles via aqueous based electro chemical route for heterogeneous electro-Fenton removal of azo dyes, J. Taiwan Inst. Chem. Eng. 71 (2017) 91–105.

[168] A.G. Akerdi, Z. Es'haghzade, S.H. Bahrami, M. Arami, Comparative study of GO and reduced GO coated graphite electrodes for decolorization of acidic and basic dyes from aqueous solutions through heterogeneous electro-Fenton process, J.

Environ. Chem. Eng. 5 (2017) 2313–2324.

[169] E. Bocos, M. Pazos, M.A. Sanromán, Electro-Fenton decolourization of dyes in batch mode by the use of catalytic activity of iron loaded hydrogels: heterogeneous electro-Fenton by using of iron-polyacrylamide hydrogels, J. Chem. Technol. Biotechnol. 89 (2014) 1235–1242.

[170] A. Babuponnusami, K. Muthukumar, Removal of phenol by heterogenous photo electro Fenton-like process using nano-zero valent iron, Sep. Purif. Technol. 98 (2012) 130–135.

[171] W. Liu, Z. Ai, L. Zhang, Design of a neutral three-dimensional electro-Fenton system with foam nickel as particle electrodes for wastewater treatment, J. Hazard. Mater. 243 (2012) 257–264.

[172] Z. Wang, J. Qi, Y. Feng, K. Li, X. Li, Preparation of catalytic particle electrodes from steel slag and its performance in a three-dimensional electrochemical oxidation system, J. Ind. Eng. Chem. 20 (2014) 3672–3677.

[173] W. He, Q. Ma, J. Wang, J. Yu, W. Bao, H. Ma, A. Amrane, Preparation of novel kaolin-based particle electrodes for treating methyl orange wastewater, Appl. Clay Sci. 99 (2014) 178–186.

[174] N. Qiao, J. Chang, M. Hu, H. Ma, Novel bentonite particle electrodes based on Fenton catalyst and its application in orange II removal, Desalination Water Treat. (2015) 1–9.

[175] H. Chu, Z. Wang, Y. Liu, Application of modified bentonite granulated electrodes for advanced treatment of pulp and paper mill wastewater in three-dimensional electrode system, J. Environ. Chem. Eng. 4 (2016) 1810–1817.

[176] J. Jiang, G. Li, Z. Li, X. Zhang, F. Zhang, An Fe–Mn binary oxide (FMBO) modified electrode for effective electrochemical advanced oxidation at neutral pH, Electrochim. Acta 194 (2016) 104–109.

[177] A. Khataee, S. Sajjadi, A. Hasanzadeh, B. Vahid, S.W. Joo, One-step preparation of nanostructured martite catalyst and graphite electrode by glow discharge plasma for heterogeneous electro-Fenton like process, J. Environ. Manage. 199 (2017) 31–45.

[178] C. Zhang, L. Zhou, J. Yang, X.M. Yu, Y.H. Jiang, M.H. Zhou, Nanoscale zero-valent iron/AC as heterogeneous fenton catalyst in three-dimensional electrode system, Environ. Sci. Pollut. Res. 21 (2014) 8398–8405.

[179] B. Hou, H. Han, S. Jia, H. Zhuang, P. Xu, K. Li, Three-dimensional heterogeneous electro-Fenton oxidation of biologically pretreated coal gasification wastewater using sludge derived carbon as catalytic particle electrodes and catalyst, J. Taiwan Inst. Chem. Eng. 60 (2016) 352–360.

[180] Y. Liu, Z. Yu, Y. Hou, Z. Peng, L. Wang, Z. Gong, J. Zhu, D. Su, Highly efficient Pd-Fe/Ni foam as heterogeneous Fenton catalysts for the three-dimensional electrode system, Catal. Commun. 86 (2016) 63–66.

[181] Y. Qin, M. Sun, H. Liu, J. Qu, AuPd/Fe₃O₄-based three-dimensional electrochemical system for efficiently catalytic degradation of 1-butyl-3-methylimidazolium hexafluorophosphate, Electrochim. Acta 186 (2015) 328–336.

[182] Q. Tang, D. Wang, D. Yao, C. Yang, Y. Sun, Heterogeneous electro-Fenton oxidation of p-nitrophenol with a reusable fluffy clump steel wire, Desalin. Water Treat. 57 (2016) 15475–15485.

[183] A. Özcan, Y. Şahin, A. Savaş Koparal, M.A. Oturan, Carbon sponge as a new cathode material for the electro-Fenton process: comparison with carbon felt cathode and application to degradation of synthetic dye basic blue 3 in aqueous medium, J. Electroanal. Chem. 616 (2008) 71–78.

[184] K. Kato, K. Kano, T. Ikeda, Electrochemical characterization of carbon felt electrodes for bulk electrolysis and for biocatalyst-assisted electrolysis, J. Electrochem. Soc. 147 (2000) 1449–1453.

[185] N. Oturan, J. Wu, H. Zhang, V.K. Sharma, M.A. Oturan, Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: effect of electrode materials, Appl. Catal. B Environ. 140–141 (2013) 92–97.

[186] A. Alvarez-Gallegos, D. Pletcher, The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell, part 1. The electrosynthesis of hydrogen peroxide in aqueous acidic solutions, Electrochim. Acta 44 (1998) 853–861.

[187] G. Coria, T. Pérez, I. Sirés, J.L. Nava, Mass transport studies during dissolved oxygen reduction to hydrogen peroxide in a filter-press electrolyzer using graphite felt, reticulated vitreous carbon and boron-doped diamond as cathodes, J. Electroanal. Chem. 757 (2015) 225–229.

[188] A. Alvarez-Gallegos, D. Pletcher, The removal of low level organics via hydrogen peroxide formed in a reticulated vitreous carbon cathode cell. Part 2: the removal of phenols and related compounds from aqueous effluents, Electrochim. Acta 44 (1999) 2483–2492.

[189] Y. Sheng, S. Song, X. Wang, L. Song, C. Wang, H. Sun, X. Niu, Electrogeneration of hydrogen peroxide on a novel highly effective acetylene black-PTFE cathode with PTFE film, Electrochim. Acta 56 (2011) 8651–8656.

[190] L. Zhuang, S. Zhou, Y. Li, T. Liu, D. Huang, In situ Fenton-enhanced cathodic reaction for sustainable increased electricity generation in microbial fuel cells, J. Power Sources. 195 (2010) 1379–1382.

[191] T. Ling, B. Huang, M. Zhao, Q. Yan, W. Shen, Repeated oxidative degradation of methyl orange through bio-electro-Fenton in bioelectrochemical system (BES), Bioresour. Technol. 203 (2016) 89–95.

[192] O. García-Rodríguez, J.A. Bañuelos, A. El-Ghenymy, L.A. Godínez, E. Brillas, F.J. Rodríguez-Valadez, Use of a carbon felt–iron oxide air-diffusion cathode for the mineralization of Malachite Green dye by heterogeneous electro-Fenton and UVA photoelectro-Fenton processes, J. Electroanal. Chem. 767 (2016) 40–48.

[193] J.S. Do, In situ oxidative degradation of formaldehyde with electrogenerated hydrogen peroxide, J. Electrochem. Soc. 140 (1993) 1632.

[194] M. Sun, X.R. Ru, L.F. Zhai, In-situ fabrication of supported iron oxides from synthetic acid mine drainage: High catalytic activities and good stabilities towards electro-Fenton reaction, Appl. Catal. B Environ. 165 (2015) 103–110.

[195] Y. Zhang, M. Gao, S.G. Wang, W. Zhou, Y. Sang, X.-H. Wang, Integrated electro-Fenton process enabled by a rotating Fe₃O₄/gas diffusion cathode for simultaneous generation and activation of H₂O₂, Electrochimica Acta. 231 (2017) 694–704.

[196] A. Xu, K. Wei, Y. Zhang, W. Han, J. Li, X. Sun, J. Shen, L. Wang, A facile-operation tubular electro-Fenton system combined with oxygen evolution reaction for flutriafol degradation: modeling and parameters optimizing, Electrochim. Acta 246 (2017) 1200–1209.

[197] K.V. Plakas, S.D. Sklari, D.A. Yiankakis, G.T. Sideropoulos, V.T. Zaspalis, A.J. Karabelas, Removal of organic micropollutants from drinking water by a novel electro-Fenton filter: pilot-scale studies, Water Res. 91 (2016) 183–194.

[198] H. Lan, J. Li, M. Sun, X. An, C. Hu, R. Liu, H. Liu, J. Qu, Efficient conversion of dimethylarsinate into arsenic and its simultaneous adsorption removal over FeCx/N-doped carbon fiber composite in an electro-Fenton process, Water Res. 100 (2016) 57–64.

[199] M. Sun, N.N. Wu, L.F. Zhai, X.R. Ru, Manipulate an air–cathode fuel cell toward recovering highly active heterogeneous electro-Fenton catalyst from the Fe(II) in acid mine drainage, Min. Eng. 84 (2015) 1–7.

[200] G. Divyapriya, I.M. Nambi, J. Senthilnathan, An innate quinone functionalized electrochemically exfoliated graphene/Fe₃O₄ composite electrode for the continuous generation of reactive oxygen species, Chem. Eng. J. 316 (2017) 964–977.

[201] L. Zhuang, S. Zhou, Y. Yuan, M. Liu, Y. Wang, A novel bioelectro-Fenton system for coupling anodic COD removal with cathodic dye degradation, Chem. Eng. J. 163 (2010) 160–163.

[202] N. Xu, Y. Zhang, H. Tao, S. Zhou, Y. Zeng, Bio-electro-Fenton system for enhanced estrogens degradation, Bioresour. Technol. 138 (2013) 136–140.

[203] X.Y. Yong, D.Y. Gu, Y.D. Wu, Z.Y. Yan, J. Zhou, X.Y. Wu, P. Wei, H.H. Jia, T. Zheng, Y.C. Yong, Bio-Electron-Fenton (BEF) process driven by microbial fuel cells for triphenyltin chloride (TPTC) degradation, J. Hazard. Mater. 324 (2017) 178–183.

[204] N. Birjandi, H. Younesi, A.A. Ghoreyshi, M. Rahimnejad, Electricity generation through degradation of organic matters in medicinal herbs wastewater using bio-electro-Fenton system, J. Environ. Manage. 180 (2016) 390–400.

[205] Y. Li, L. Liu, F. Yang, Destruction of tetracycline hydrochloride antibiotics by FeOOH/TiO₂ granular activated carbon as expanded cathode in low-cost MBR/MFC coupled system, J. Membr. Sci. 525 (2017) 202–209.

[206] Y. Li, A. Lu, H. Ding, X. Wang, C. Wang, C. Zeng, Y. Yan, Microbial fuel cells using natural pyrrhotite as the cathodic heterogeneous Fenton catalyst towards the degradation of biorefractory organics in landfill leachate, Electrochem. Commun. 12 (2010) 944–947.

[207] Y. Fan, Z. Ai, L. Zhang, Design of an electro-Fenton system with a novel sandwich film cathode for wastewater treatment, J. Hazard. Mater. 176 (2010) 678–684.

[208] H. Maleki, Recent advances in aerogels for environmental remediation applications: a review, Chem. Eng. J. 300 (2016) 98–118.

[209] S.S. Kistler, Coherent expanded-aerogels, J. Phys. Chem. 36 (1931) 52–64.

[210] S.S. Kistler, Coherent expanded aerogels and Jellies, Nature 127 (1931) 741.

[211] A.M. Anderson, M.K. Carroll, Hydrophobic silica aerogels: review of synthesis, properties and applications, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 47–77.

[212] J.S. Falcone (Ed.), Soluble Silicates, American Chemical Society, Washington, D. C, 1982.

[213] A. Soleimani Dorcheh, M.H. Abbasi, Silica aerogel; synthesis, properties and characterization, J. Mater. Process. Technol. 199 (2008) 10–26.

[214] N. Hüsing, U. Schubert, Aerogels—airy materials: chemistry, structure, and properties, Angew. Chem. Int. Ed. 37 (1998) 22–45.

[215] M. Moner-Girona, A. Roig, E. Molins, J. Llibre, Sol-gel route to direct formation of silica aerogel microparticles using supercritical solvents, J. Sol–Gel Sci. Technol. 26 (2003) 645–649.

[216] T.F. Baumann, A.E. Gash, S.C. Chinn, A.M. Sawvel, R.S. Maxwell, J.H. Satcher, Synthesis of high-surface-area alumina aerogels without the use of alkoxide precursors, Chem. Mater. 17 (2005) 395–401.

[217] H. Hirashima, Preparation of TiO₂ aerogels-like materials under ambient pressure, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 145–153.

[218] A.C. Pierre, A. Rigacci, SiO₂ aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 21–45.

[219] S. Mulik, C. Sotiriou-Leventis, Resorcinol–formaldehyde aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 215–234.

[220] A. Rigacci, P. Achard, Cellulosic and polyurethane aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 191–214.

[221] T. Horikawa, J. Hayashi, K. Muroyama, Size control and characterization of spherical carbon aerogel particles from resorcinol–formaldehyde resin, Carbon 42 (2004) 169–175.

[222] M.A. Worsley, J.H. Satcher, T.F. Baumann, Synthesis and characterization of monolithic carbon aerogel nanocomposites containing double-walled carbon nanotubes, Langmuir 24 (2008) 9763–9766.

[223] M.A. Worsley, P.J. Pauzauskie, T.Y. Olson, J. Biener, J.H. Satcher, T.F. Baumann, Synthesis of graphene aerogel with high electrical conductivity, J. Am. Chem. Soc. 132 (2010) 14067–14069.

[224] D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, Design and preparation of porous polymers, Chem. Rev. 112 (2012) 3959–4015.

[225] S.L. Brock, H. Yu, Chalcogenide aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp.

367–384.

[226] I. Selmer, C. Kleemann, U. Kulozik, S. Heinrich, I. Smirnova, Development of egg white protein aerogels as new matrix material for microencapsulation in food, J. Supercrit. Fluids 106 (2015) 42–49.

[227] L. Ratke, Monoliths and fibrous cellulose aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011, pp. 173–190.

[228] M. Betz, C.A. García-González, R.P. Subrahmanyam, I. Smirnova, U. Kulozik, Preparation of novel whey protein-based aerogels as drug carriers for life science applications, J. Supercrit. Fluids 72 (2012) 111–119.

[229] Y. Kong, Y. Zhong, X. Shen, S. Cui, M. Yang, K. Teng, J. Zhang, Facile synthesis of resorcinol–formaldehyde/silica composite aerogels and their transformation to monolithic carbon/silica and carbon/silicon carbide composite aerogels, J. Non-Cryst. Solids. 358 (2012) 3150–3155.

[230] L. Kong, A.T. Lemley, Kinetic modeling of 2,4-dichlorophenoxyacetic acid (2,4-D) degradation in soil slurry by anodic Fenton treatment, J. Agric. Food Chem. 54 (2006) 3941–3950.

[231] Y. Kong, X. Shen, S. Cui, M. Fan, Preparation of monolith SiC aerogel with high surface area and large pore volume and the structural evolution during the preparation, Ceram. Int. 40 (2014) 8265–8271.

[232] N. Leventis, A. Sadekar, N. Chandrasekaran, C. Sotiriou-Leventis, Click synthesis of monolithic silicon carbide aerogels from polyacrylonitrile-coated 3D silica networks, Chem. Mater. 22 (2010) 2790–2803.

[233] A. Cabañas, E. Enciso, M.C. Carbajo, M.J. Torralvo, C. Pando, J.A.R. Renuncio, Synthesis of SiO2 -aerogel inverse opals in supercritical carbon dioxide, Chem. Mater. 17 (2005) 6137–6145.

[234] J. Zou, J. Liu, A.S. Karakoti, A. Kumar, D. Joung, Q. Li, S.I. Khondaker, S. Seal, L. Zhai, Ultralight multiwalled carbon nanotube aerogel, ACS Nano 4 (2010) 7293–7302.

[235] H.X. Zhang, C. Wang, J.Y. Wang, J.J. Zhai, W.B. Cai, Carbon-supported Pd−Pt nanoalloy with low Pt content and superior catalysis for formic acid electro-oxidation, J. Phys. Chem. C 114 (2010) 6446–6451.

[236] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon aerogels for catalysis applications: an overview, Carbon 43 (2005) 455–465.

[237] H. Bi, Z. Yin, X. Cao, X. Xie, C. Tan, X. Huang, B. Chen, F. Chen, Q. Yang, X. Bu, X. Lu, L. Sun, H. Zhang, Carbon fiber aerogel made from raw cotton: a novel, efficient and recyclable sorbent for oils and organic solvents, Adv. Mater. 25 (2013) 5916–5921.

[238] H. Bi, X. Huang, X. Wu, X. Cao, C. Tan, Z. Yin, X. Lu, L. Sun, H. Zhang, Carbon microbelt aerogel prepared by waste paper: an efficient and recyclable sorbent for oils and organic solvents, Small 10 (2014) 3544–3550.

[239] H. Chen, X. Wang, J. Li, X. Wang, Cotton derived carbonaceous aerogels for the efficient removal of organic pollutants and heavy metal ions, J. Mater. Chem. A 3 (2015) 6073–6081.

[240] H. Maleki, L. Durães, A. Portugal, An overview on silica aerogels synthesis and different mechanical reinforcing strategies, J. Non-Cryst. Solids 385 (2014) 55–74.

[241] H. Maleki, L. Durães, A. Portugal, Development of mechanically strong ambient pressure dried silica aerogels with optimized properties, J. Phys. Chem. C 119 (2015) 7689–7703.

[242] M. Wu, Y. Jin, G. Zhao, M. Li, D. Li, Electrosorption-promoted photodegradation of opaque wastewater on a novel TiO2 /carbon aerogel electrode, Environ. Sci. Technol. 44 (2010) 1780–1785.

[243] M. Paskevicius, H.Y. Tian, D.A. Sheppard, C.J. Webb, M.P. Pitt, E.M. Gray, N.M. Kirby, C.E. Buckley, Magnesium hydride formation within carbon aerogel, J. Phys. Chem. C 115 (2011) 1757–1766.

[244] J. Biener, M. Stadermann, M. Suss, M.A. Worsley, M.M. Biener, K.A. Rose, T.F. Baumann, Advanced carbon aerogels for energy applications, Energy Environ. Sci. 4 (2011) 656.

[245] G. Lv, D. Wu, R. Fu, Performance of carbon aerogels particle electrodes for the aqueous phase electro-catalytic oxidation of simulated phenol wastewaters, J. Hazard. Mater. 165 (2009) 961–966.

[246] C. Brinker, K. Keefer, D. Schaefer, C. Ashley, Sol-gel transition in simple silicates, J. Non-Cryst. Solids 48 (1982) 47–64.

[247] C.J. Brinker, D.R. Tallant, E.P. Roth, C.S. Ashley, Sol-gel transition in simple silicates, J. Non-Cryst. Solids 82 (1986) 117–126.

[248] C.J. Brinker, K.D. Keefer, D.W. Schaefer, R.A. Assink, B.D. Kay, C.S. Ashley, Sol-gel transition in simple silicates II, J. Non-Cryst. Solids 63 (1984) 45–59.

[249] G.M. Pajonk, A. Venkateswara Rao, N.N. Parvathy, E. Elaloui, Microstructural characterization of silica aerogels using scanning electron microscopy, J. Mater. Sci. 31 (1996) 5683–5689.

[250] A.V. Rao, G.M. Pajonk, U.K.H. Bangi, A.P. Rao, M.M. Koebel, Sodium silicate based aerogels via ambient pressure drying, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 103–124.

[251] H. Maleki, L. Durães, A. Portugal, Synthesis of lightweight polymer-reinforced silica aerogels with improved mechanical and thermal insulation properties for space applications, Microporous Mesoporous Mater. 197 (2014) 116–129.

[252] H. Maleki, L. Durães, A. Portugal, Synthesis of mechanically reinforced silica aerogels via surface-initiated reversible addition-fragmentation chain transfer (RAFT) polymerization, J. Mater. Chem. A 3 (2015) 1594–1600.

[253] X. Liu, Y. Zhou, J. Zhang, L. Tang, L. Luo, G. Zeng, Iron containing metal–organic frameworks: structure, synthesis, and applications in environmental remediation, ACS Appl. Mater. Interfaces 9 (2017) 20255–20275.

[254] X. Xiong, N. Ji, C. Song, Q. Liu, Preparation functionalized graphene aerogels as air cleaner filter, Procedia Eng. 121 (2015) 957–960.

[255] S.F. Chin, A.N. Binti Romainor, S.C. Pang, Fabrication of hydrophobic and magnetic cellulose aerogel with high oil absorption capacity, Mater. Lett. 115 (2014) 241–243.

[256] L.L. Hench, J.K. West, The sol–gel process, Chem. Rev. 90 (1990) 33–72.

[257] P.F. James, Science of ceramic chemical processing, Polymer. 28 (1987) 1233.

[258] D.Y. Nadargi, S.S. Latthe, A. Venkateswara Rao, Effect of post-treatment (gel aging) on the properties of methyltrimethoxysilane based silica aerogels prepared by two-step sol–gel process, J. Sol–Gel Sci. Technol. 49 (2009) 53–59.

[259] J. Estella, J.C. Echeverría, M. Laguna, J.J. Garrido, Effects of aging and drying conditions on the structural and textural properties of silica gels, Microporous Mesoporous Mater. 102 (2007) 274–282.

[260] R.A. Strøm, Y. Masmoudi, A. Rigacci, G. Petermann, L. Gullberg, B. Chevalier, M.-A. Einarsrud, Strengthening and aging of wet silica gels for up-scaling of aerogel preparation, J. Sol–Gel Sci. Technol. 41 (2007) 291–298.

[261] M.-A. Einarsrud, E. Nilsen, A. Rigacci, G. Pajonk, S. Buathier, D. Valette, M. Durant, B. Chevalier, P. Nitz, F. Ehrburger-Dolle, Strengthening of silica gels and aerogels by washing and aging processes, J. Non-Cryst. Solids 285 (2001) 1–7.

[262] G. Zhang, A. Dass, A.-M.M. Rawashdeh, J. Thomas, J.A. Counsil, C. Sotiriou-Leventis, E.F. Fabrizio, F. Ilhan, P. Vassilaras, D.A. Scheiman, L. McCorkle, A. Palczer, J.C. Johnston, M.A. Meador, N. Leventis, Isocyanate-crosslinked silica aerogel monoliths: preparation and characterization, J. Non-Cryst. Solids 350 (2004) 152–164.

[263] M.A.B. Meador, Improving elastic properties of polymer-reinforced aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011, pp. 315–334.

[264] N. Leventis, Three-dimensional core-shell superstructures: mechanically strong aerogels, Acc. Chem. Res. 40 (2007) 874–884.

[265] J. Shen, D.Y. Guan, Preparation and application of carbon aerogels, in: M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), Aerogels Handb. Springer New York, New York, NY, 2011pp. 813–831.

[266] T. Horikawa, J. Hayashi, K. Muroyama, Size control and characterization of spherical carbon aerogel particles from resorcinol–formaldehyde resin, Carbon 42 (2004) 169–175.

[267] H. Wakayama, Y. Fukushima, Nanoporous silica prepared with activated carbon molds using supercritical CO2, Chem. Mater. 12 (2000) 756–761.

[268] C. Jin, S. Han, J. Li, Q. Sun, Fabrication of cellulose-based aerogels from waste newspaper without any pretreatment and their use for absorbents, Carbohydr. Polym. 123 (2015) 150–156.

[269] D. Wu, R. Fu, S. Zhang, M.S. Dresselhaus, G. Dresselhaus, Preparation of low-density carbon aerogels by ambient pressure drying, Carbon 42 (2004) 2033–2039.

[270] D. Wu, R. Fu, Synthesis of organic and carbon aerogels from phenol–furfural by two-step polymerization, Microporous Mesoporous Mater. 96 (2006) 115–120.

[271] R.W. Pekala, Organic aerogels from the polycondensation of resorcinol with formaldehyde, J. Mater. Sci. 24 (1989) 3221–3227.

[272] R.W. Pekala, C.T. Alviso, J.D. LeMay, Organic aerogels: microstructural dependence of mechanical properties in compression, J. Non-Cryst. Solids 125 (1990) 67–75.

[273] X. Wu, X. Yang, D. Wu, R. Fu, Feasibility study of using carbon aerogel as particle electrodes for decoloration of RBRX dye solution in a three-dimensional electrode reactor, Chem. Eng. J. 138 (2008) 47–54.

[274] Y. Wang, H. Zhao, G. Zhao, Highly ordered mesoporous Fe3O4 @carbon embedded composite: high catalytic activity, wide pH range and stability for heterogeneous electro-Fenton, Electroanalysis 28 (2016) 169–176.

[275] H. Zhao, L. Qian, Y. Chen, Q. Wang, G. Zhao, Selective catalytic two-electron O2 reduction for onsite efficient oxidation reaction in heterogeneous electro-Fenton process, Chem. Eng. J. 332 (2018) 486–498.

[276] Q. Peng, H. Zhao, L. Qian, Y. Wang, G. Zhao, Design of a neutral photo-electro-Fenton system with 3D-ordered macroporous Fe2O3/carbon aerogel cathode: high activity and low energy consumption, Appl. Catal. B Environ. 174–175 (2015) 157–166.

[277] W. Yang, M. Zhou, J. Cai, L. Liang, G. Ren, Ultrahigh yield of hydrogen peroxide on graphite felt cathode modified with electrochemically exfoliated graphene, J. Mater. Chem. A 5 (2017) 8070–8080.

[278] M. Zhou, L. Zhou, L. Liang, F. Yu, W. Yang, Cathode modification to improve electro-Fenton performance, The Handbook of Environmental Chemistry 61 Springer, Singapore, 2017, pp. 175–203, http://dx.doi.org/10.1007/698_2017_58.